



# Journal of the Society of Chemical Industry.

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## The Society of Chemical Industry.

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## Official Notice.

### ANNUAL GENERAL MEETING, 1915.

In accordance with the provisions of By-law 34, notice is hereby given that the Annual General Meeting will be held at the Municipal School of Technology, Manchester, at 10.30 a.m. on Wednesday, July 14th, 1915. A programme of the proceedings will be issued later.

In accordance with the provisions of By-law 24, those members whose names are printed in *italics* in the List of Council will retire from their respective offices at the forthcoming Annual Meeting.

Dr. C. C. Carpenter has been nominated to the office of President under By-law 20; Prof. G. G. Henderson has been nominated a Vice-President under By-law 20; Prof. E. C. C. Baly, F.R.S., Mr. R. H. Clayton, and Mr. Julius Hübner have been nominated Vice-Presidents under By-law 21, and Mr. Thos. Tyrer and Dr. R. Messel, F.R.S., have been reappointed Hon. Treasurer and Hon. Foreign Secretary respectively.

Members are requested to nominate, on or before May 22nd next, fit and proper persons to fill four vacancies among the Ordinary Members of Council. Forms for this purpose can be obtained from the Secretary of the Society.

By-law 23:—An Ordinary Member of Council shall be nominated by ten or more members upon Form B in the Schedule, a copy of which form shall be furnished by the Secretary upon the written or verbal request of any member, but a member shall not be eligible to sign more than one such nomination form, and the member nominated shall sign the declaration set forth on the form. A nomination shall be declared invalid by the Council if:

a. The member thereon nominated is disqualified for election, or ineligible to be elected, as provided by the By-laws.

b. The nomination is not made on the authorised printed form or substantially not in the manner directed thereon.

c. The nomination form is signed by less than ten members not disqualified or not ineligible to nominate as provided by the By-laws.

d. The nomination form is not received before or upon the day appointed therefor.

e. The member nominated has not signed the declaration printed upon the form.

A member whose nomination aforesaid is declared to be invalid, shall receive notice thereof from the Secretary, and shall not be submitted for election.

CHARLES G. CRESSWELL,

Secretary.

### Birmingham Section.

Meeting held at Birmingham University, on Thursday, April 15th, 1915.

MR. H. T. PINNOCK IN THE CHAIR.

### POSSIBLE SOURCES OF POTASH.

BY CHARLES G. CRESSWELL.

Although sodium salts will replace potassium salts in many cases, for some important processes potassium salts are still essential or present practical advantages. Potash is wanted in the manufacture of soft soap and crystal and hard glass, as a frit or glaze for pottery, as a fertiliser, for

pyrotechny, explosives, and matches, and for preserving food; and in a less degree in tanning (as chrome alum), printing (as chlorate and ferro-arsenate), photography, and medicine. In medicine the chief advantage of potassium salts lies in their superior rapidity of absorption and excretion, but in nearly every case the corresponding sodium salts can replace them. The uses of potash in the laboratory are well known.

Stassfurt salts are not separately distinguished in the "Annual Statement of Trade of the United Kingdom," nor were they specifically enumerated in the German official Trade Returns prior to 1890. The first allusions to them occur in British patent records in the year 1863 (Klemm, Eng. Pat. 1776 of 1863). The exports from Germany to the United Kingdom since 1890 have been as follows:—

Year.	Tons.	Value £.
1890 .....	33,731	48,400
1895 .....	31,648	39,550
1900 .....	28,191	34,550
1905 .....	32,461	34,500
1910 .....	52,705	65,900

The German Potash Syndicate was founded in 1879 after 22 years of competition and limited consumption. In 1879 the output of crude salts was 768,971 metric tons, while in 1902 it had increased to 3,250,835 tons. Simultaneously prices improved, due to a systematic propaganda among agriculturists.

In 1911 the Syndicate extracted 9,706,507 tons of crude salts, of which the United States took 1,002,326 tons for agriculture and 22,828 tons for industrial purposes. The German Government allow only one half of the output to be exported, so that Germany has nearly 5,000,000 tons of crude salts for home consumption. There are at present 115 mines; 510 executive officers and 37,000 foremen and labourers are employed.

In reply to a question as to how far a reduction in the price of crude salts would affect their consumption in the chemical industry, Grüneberg (this J., 1882, 25) stated that it was doubtful if the price of crude salts—within limits—could affect the industrial consumption of potash; such industries could well afford to pay for it. Stassfurt, he said, ruled the world. Cheap potash salts were good for the German chemical industry, and any attempt to raise the price by monopoly would involve loss of business. As a fact, competition among the mines kept down prices.

In 1902 the United States obtained control of certain mines, and already in 1906 there were signs of over-production, seeing that of the 36 mines belonging to the Syndicate, 31 were sinking new shafts. In 1909 the Syndicate was provisionally renewed for another year. The acquisition of two groups of mines by the International Agricultural Corporation of America created some difficulty. Negotiations were opened for taking over their contracts under a threat that, if the Syndicate were not renewed, Germany would levy an export duty on potash equal to about £1 per ton on concentrated salts. This threat failed, and the Syndicate started to undersell the Americans. In May, 1910, Germany passed a law making all potash mines members of a pool under Government control, with a strictly limited right of output. Maximum prices for domestic distribution were fixed, and export prices were not to exceed them. The United States protested vigorously but to no purpose. By this time the number of mines had risen to 80, and profits were much attenuated. The United States resented the limitations placed by Germany on the output of mines belonging to American Corporations, and started to search for

new sources of supply. This is the reason why there is so much recent literature on new sources of potash.

On August 31st last the offices of the Syndicate were closed, and it was stated that the mines were not in a condition to be worked, the shafts being filled with water. About the same date, in London, kainit, which sold last spring for £2 per ton, was quoted at £4, caustic potash went up to £4 per cwt., and potassium carbonate was quoted at about £65 per ton. Little more, if any, Stassfurt salts are likely to be available till the end of the war. To medicine this is not very serious, but to agriculture it comes somewhat as a shock. British agriculture, however, did without these salts for many years. For a time it must do without them now, and chemists must cudgel their brains to find other sources of supply. The potash situation has been further complicated by the recent embargo placed by the German Government on the export of potash. At the present time (March), the Federal Council has under consideration a proposal to increase the home prices for potash to what they were before the Potash Act of 1910. The Potash Syndicate calculates a production of 949,000 tons of pure potash for 1915; 563,000 tons for home consumption and 386,000 tons for export. In 1914 the production was 1,167,000 tons; the exports are said to have been 531,000 tons, and the home consumption 636,000 tons.

In the course of this paper, the rise and fall of certain potash industries will be recorded. These changes must not hastily be attributed to apathy on the part of the British manufacturer. The kelp industry was carried on for years at a loss, because its cessation meant starvation in the

crystallises out abundantly, and the density falls to 32°–33° B. The next day, when the water warms up again, the salts deposited at night do not redissolve, and the layer of Epsom salts is covered by a fresh deposit of mixed salts. After a period of these alternations, the mixed salts, containing about 40–45% of Epsom salts and 50–55% of common salt, are collected, while the mother liquors are gathered in large cement tanks and refrigerated.

This separates the potassium salts as carnallite ( $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ); this is treated with half its weight of cold water, which dissolves the magnesium chloride with a little potassium chloride, leaving 75% of potassium chloride. The solution is returned to the lagoons, and the crystals of the potassium chloride are centrifuged. One cubic metre of sea water at 28° B., corresponding to 75 cubic metres of ordinary sea water, gives by this process 10 kilos. of potassium chloride. The climate has much influence on the success of this process. The Dead Sea in Palestine and lakes in the tropics without outlets, such as Lake Chad in Nigeria, contain considerable stores of potash salts. The Caspian Sea and Sea of Aral in Russia, and the Rann of Cutch in India are worth examination. Near Yarmouth in the Isle of Wight are remains of such lagoons, though the collection of common salt was their main object.

Heraclitus (J. Chem. Soc., Vol. 2, 336) states that the waters of the Dead Sea contain in parts per million: sodium 47,908; potassium 6385; and bromine 2167.7.

The following table gives the contents of sodium and potassium salts in normal seas in parts per million:—

Locality.	Venice Lagoons.	Bay of Leghorn.	Mediterranean (Cette).	Pacific I.	Pacific II.	Atlantic I.	Atlantic II.	North Sea.	Red Sea.	Dead Sea.
Sp. gr. ...	1.0184	1.0231	1.0258	1.0264	1.0260	1.0244	1.0287	—	1.03060	—
NaCl .....	22,346	26,191	29,424	25,885	25,887	26,442	29,554	25,513	30,300	108,530
KCl .....	833	1111	505	—	—	—	—	—	2880	13,468
$\text{K}_2\text{SO}_4$ ...	—	—	—	1359	1327	1499	1810	1529	2950	—

Western Highlands and Islands. Given constant over-production of Stassfurt salts, an imperative need for outlet, untiring Government assistance in every form, and a legion of commercial travellers ever thrusting them before consumers, what chance of existence had the private competitor with his potash in dribblets from kelp, molasses, wool scouring, felspar, and sea-water?

#### Potash from sea water.

All the potash washed off the land eventually finds its way into the sea. From sea water it may be obtained direct or through the agency of sea-weed. Comparatively little attention has been paid to its direct extraction, but it is worth trying, especially where the sun's rays are sufficiently abundant. Sir James Dewar in his presidential address at Glasgow (this J., 1888, p. 479) referred to Balard's process of extraction as being used by M. Pechiney at that date. It appears, however (International Exhibition of 1862, Reports of the Juries, Class II., 48–50) that after 1860 a process came into use which was a combination of Balard's process with that of M. Merle, partner of M. Pechiney. In this process, sea water is concentrated in lagoons by sun action to 28° B. At the Salin Giraud there are 123 acres of earthen lagoons and 40 acres of cemented areas. During the day the sea water deposits salt mixed with a little magnesium sulphate and gradually concentrates to 35° B. On clear nights, radiation cools the liquor to such an extent that magnesium sulphate with 7 equivalents of water

#### Potash from sea-weed (kelp).

Sea-weed contains on an average 80.41% of water, 9.25% of organic matter (0.45% N) and 10.31% of ash ( $\text{K}=1.95$ ,  $\text{P}_2\text{O}_5=0.47$ ) (Macadam, this J., 1888, 79). When air-dried the giant kelps of the Pacific lose 85% of their weight and then contain 10–15% of potash (as KCl) as well as 1% of nitrogen and 0.5% of phosphoric acid. Experiments made by the United States Bureau of Soils with wheat (Circ. No. 76) showed an increased growth of 31% on one soil and 23% on another, about equal to that produced by potassium chloride but slightly less than by potassium sulphate. Green kelp is too bulky to be transported any distance for fertilising. Cameron (this J., 1912, 227) estimates the possible supply from Pacific kelps as 1,000,000 tons per annum. Balch (this J., 1910, 150) states that one ton of air dried kelp yields 500 lb. of potassium carbonate and 3 lb. of iodine. He suggests collection by properly fitted ships, drying on shore until efflorescence appears (by which time the weed is dry enough without being too hard to press into bales), carbonisation to a point where the carbon is rendered insoluble, and lixiviation.

The algae *Nereocystis* and *Macrocystis* absorb far more potash than soda from the sea, and the efflorescence consists of nearly pure potassium chloride. Their stems contain the most potash. (Merz, this J., 1914, 134) but they are low in iodine. Lindemuth (this J., 1914, 1086) states that freshly cut kelp does not lose potassium chloride when immersed in sea water for a period up to 13

hours. The ash of the rock weed "sea lettuce" contains 45% of KCl. Its presence in kelp is desirable but it would not pay to collect it separately. Up to 1885, Japan imported potash and iodine; since then she has learnt to extract them from kelp, and now sends potash to Europe, and iodine valued at £192,000 annually to the United States.

The kelp industry of Scotland is of very ancient date and is intimately connected with that of glass. The Celtic vitrified forts, which have puzzled archaeologists, arose in this way. Ramparts of sand were covered with dry sea-weed and the sea-weed set on fire. On the vitrified layer thus formed more sand was piled and the operation repeated until a vitreous rampart of considerable height and hardness was obtained. One of these forts may be seen not far from Connell Ferry in Argyllshire.

In olden times the sea-weed, dried as much as the climate would permit, was burnt in the open and the charcoal leached; considerable loss of salts resulted. As early as 1767, Delaval (Eng. Pat. 270) proposed burning the wet weed in reverberatory kilns by the aid of coal or wood. There were one or two patents faintly modelled on Le Blanc's soda process, but until Stanford's time men's minds were devoted to soda. In 1861 (Eng. Pat. 1411), in place of burning sea-weed in the open, Stanford dried it and pressed it into cakes, and destructively distilled it. The charcoal was withdrawn into closely-covered iron boxes to cool, leached and treated as usual for potash and iodides. The distillate gave gas and a tar water which yielded ammonia and other useful bodies.

Gignou and Gagnage (Eng. Pat. 2741 of 1865) proposed to crush and press *Fucus giganteus* and *Zostera maritima*, preferably while wet, so as to extract the salts and nitrogenous organic matter. They steeped the residual pulp in a solution of sodium carbonate, and again pressed it to deprive it of the greater part of the lye, which they used again. The solid residue was to be used for the manufacture of paper.

After this potash became of secondary importance and iodides only were sought. In 1881 (Eng. Pat. 142) Stanford leached the kelp with hot or cold water, boiled down the liquor, and carbonised the extract for potash and iodine. The residual pulp boiled with alkali gave alginate, which had only a moderate success. Soon afterwards even the iodine ceased to be profitable and the works were at last closed down.

The action of the German Government in regard to Stassfurt salts stimulated the United States to fresh energy, and recent journals contain much literature on the extraction of potash from kelp. A recent report to the Board of Agriculture for Scotland (Cd. 7564; this J., 1914, 919) describes the American methods of collection and treatment, and the article on "Iodine" in Thorpe's Dictionary, written by Stanford and revised by Prof. Henderson, affords much valuable information. The Columbia Chemical Co., of Los Angeles, Cal., U.S.A., invites correspondence from those interested.

The Board of Agriculture for Scotland, 29, St. Andrew Square, Edinburgh, has been taking steps to increase the output of kelp this season. At present, kelp is purchased by two Scottish firms, and names of other purchasers are asked for. Sea transport from the Islands and Highlands, where it is collected, is available.

Boberg and Testrup (Eng. Pat. 1700 of 1914, this J., 1915, 227) mince and pulp kelp, freed from occluded air, and heat in closed vessels to 170° C. for 20 minutes. The mass now yields a firm press cake. The liquor contains 70% of the original alkali salts, 90% of the iodine, 33% of the nitrogen, and 10% of the organic matter.

The U.S. Bureau of Soils considers that £10,000 would be sufficient to instal plant for producing potash from kelp on a small commercial scale, and Mr. H. S. Gale expresses the opinion that the kelp beds afford the only really promising sources of potash in commercial quantities (Oil, Paint, and Drug Rep., Feb. 8, 1915).

#### Plant and wood ashes.

This was the earliest source of potash, and in the sixteenth and seventeenth centuries "Muscovy ashes" were highly esteemed by soap boilers; they contained lime. The Board of Trade states that two cargoes (200—300 tons) a month had been coming from South Russia for some time past, but at present shipment is stopped. Potash is still made from wood ashes in the north-west of the United States and in Canada. In 1894 Canada produced 1936 barrels (this J., 1899, 190). In 1898 this had fallen to 1080 barrels, due to the adulteration with soda salts and the abolition of compulsory inspection. There is always some demand for it for soft soap making.

As early as 1802 Hudson (Eng. Pat. 2586) drew attention to "soapers' waste ashes," tanners' bark, bean and other straw, fern, furze, and broom, as well as kelp, as sources of potash. J. C. Umney (this J., 1914, 1046) suggests co-operation for the collection and incineration of many waste sea and land plants, such as furze, bracken and hedge-clippings. He gives the potassium contents of various ashes: bracken 60%, *Boletus edulis* 50—57%, *Agaricus velutipes* 78%, *Hypnum Schroberi* 28—30%, groundsel 43.5%, broom 33%, and *Euphorbia amygdaloides* 39%. A conference has recently been held in Edinburgh under the auspices of the Board of Agriculture on this subject and a Committee appointed to take up the matter. The annual consumption in Scotland is given as about 25,000 tons of 10—15% potash and 500 tons of high grade salts 40—50% (Ch. Tr. Jnl., Dec. 12th, 1914). Quintenne (this J., 1905, 1302) states that mangrove trees growing in fresh water marshes are rich in potash salts. There are many noxious weeds and inconvenient growths all over the world, the ash of which might be examined for potash, such as the prickly pear in Australia, the sudd of the Nile, the reeds and rushes, bracken, and brushwood.

In the Caucasus there are 24 factories producing potash from the stems of sunflowers. In 1907, 14,500 tons was produced.

#### Saltpetre.

In the Agricultural Ledger for 1905 (pp. 17—48, this J., 1905, 1170) Dr. D. Hooper discusses nitrification with special reference to conditions obtaining in India. He also gives an account of the districts where nitrous earths occur and where the salt is manufactured, describes process of manufacture, and gives analysis of crude and pure salts and by-products. J. W. Leather has also reported to the Government of India on this subject. The supply of saltpetre from India is increasing (March, 1915), and the production may assume much larger proportions. There are numerous caves in India and other countries where it has accumulated, and the formation of nitrates in the soil is continuous. A process has been perfected recently in India for avoiding waste. The plant for a daily production of 2400 lb. costs only £200, and a product of 94% purity is secured.

Potassium nitrate invariably accompanies the sodium compound in the deposits of Chile, 3—5% of the former to about 25—50% of the latter. At Tacunga in Peru, and at Cochabamba in Bolivia, deposits of saltpetre of some importance have been met with (T. H. Norton, U.S. Dept. of Comm. and Labour. Special Agent's Series, No. 52).

*Potash lakes and deposits.*

The Board of Trade Journal of Dec. 12th, 1907 (this J., 1907, 1278), stated that large tracts of ground between Torrelavega and Cabezon de la Sal (near Santander in Spain) had been taken up by a Belgian firm of alkali manufacturers. Borings proved the presence of sodium and potassium salts in quantity, which were to be treated locally.

A salt field in the bed of a Miocene lake has recently been found at Cardona, on the borders of Barcelona and Lerida. The Stassfurt Syndicate, which had already bought up all the European and other deposits on which it could lay its hands, tried to acquire this field, and the American Agricultural Chemical Co. also made offers for it. The Spanish Government, realising the importance of the question, nominated a commission of the Geological Institute of Spain to examine the deposit, and armed with their favourable report, has submitted to Parliament a measure to regulate the exploitation of these deposits (Bull. Instit. Agriculture, Rome, Jan., 1915). At a meeting of the German Geological Society of Berlin (Zent. f. d. Kunst-Industrie, XIX. 338) Prof. Schmidt stated that the deposits occurred in the tertiary deposits of the Ebro basin. They were 260 ft. thick, and contained 70 ft. of carnallite with 20% of KCl and 33 ft. of sylvine with 95% KCl. In origin they resembled those of Alsace, being secondary formations derived from more ancient saline deposits of the Triassic age. Concessions have been applied for in regard to several thousand acres in extent, not only in the province of Barcelona, but in those of Gerona, Lerida, and Huesca.

Searles Lake is the most promising potash bed yet discovered in the United States. It is in the north of San Bernardino Co., Cal., and for some twelve miles the lake bottom, as shown by borings, consists of a mass of salts about 70 ft. thick. These salts consist of sodium chloride, sulphate, carbonate, bicarbonate, and biborate, with some potassium chloride, and are coarsely crystalline and honeycombed, the spaces being filled with brine. For the first 23 ft. the deposit is mainly common salt, analysis of the brine below this showing about 4% of potassium chloride. The plan is to extract this salt from the brine which moves freely through the salts, and an output of 5 tons a day was expected within three months (this J., 1914, 919).

The Oil, Paint, and Drug Reporter (Feb. 8, 1915) states that over £300,000 has been spent in developing the Searles Lake deposits, but that a considerable addition will have to be made to the plant if potash is to be produced in commercial quantities.

It should not be forgotten that the Stassfurt deposits extend well into Upper Alsace at Cernay, near Mulhouse, and that the French are now close to that place.

A good account of the Stassfurt deposits by B. Leslie Emslie, was read before the Canadian Section in 1909 (this J., 1909, 393).

*Felspar, mica, and leucite.*

The large quantity of potash in these minerals is responsible for the number of attempts to extract it, but it must be remembered that for every 100 parts of mineral, the maximum extraction is not more than 15%, leaving some 85% of by-product, increased possibly to over 100% if lime is used to expel the potash. Orthoclase felspar has always been most in favour, though mica (muscovite), due to its being a waste product of the china clay industry in a fine state of division, has certain advantages. Leucite is comparatively scarce.

Lyell in his "Elements of Geology" gives the following content of potash in this type of mineral on the authority of Delesse, Klaproth and Rose:—

	1.	2.		
Felspar .....	12%	11%	Leucite	21%
Mica .....	10%	5.6% (black)	6% (green)	7% (reddish) 9% (white pegmatite)

The following are some analyses of felspar by Abich and Rose:—

	Theory.	a.	b.	c.
K <sub>2</sub> O .....	16.59	13.99	14.02	14.73
Na <sub>2</sub> O .....	—	1.01	1.25	trace
CaO .....	—	1.34	0.34	0.60
Al <sub>2</sub> O <sub>3</sub> .....	18.06	17.37	18.57	19.15
SiO <sub>2</sub> .....	65.35	65.67	65.72	65.52

Felspar is found in the Mourne Mountains and Wicklow in Ireland, and in Aberdeenshire in Scotland. It is plentiful in Sweden, in the United States, and in Canada.

Spiller (this J., 1882, 128) states that the granite from the Duke of Argyll's quarries in Mull consist mainly of rose-coloured felspar. That from the Mourne Mountains is mostly white, and large white crystals occur in the white granite from Lanhyvery (Cornwall), St. Barule (Isle of Man), Castlean (Penzance) and Lundy Island. Rubislaw and Cove (Aberdeen) produce almost pure felspar containing 13% potash.

Muscovite (mica) contains 11.8%, and Haughtonite from Cove (Aberdeen) 8.81%. As above-mentioned, mica is a waste, requires no crushing, and needs outlets.

Felspar in a state of minute division makes water alkaline at 220° C. Potassium tetrasilicate is probably dissolved out leaving aluminium disilicate. (Forchhammer, Pogg., 35, 353.)

Berthier states (Gmelin, III., 442) that equal weights of felspar and white marble fused in a charcoal crucible in a blast furnace yield transparent glass which is readily dissolved by acids and contains 5.9 parts of potash to 64.1 of silica.

Fuchs (ib.) states that if powdered felspar is gently ignited with lime and digested with water, or if ignited powdered felspar is boiled with milk of lime, it gives up potash to the water, the lime taking its place.

Felspar is used both as a glaze and glass-forming ingredient in porcelain. "Cornish Stone" is a granite in which felspar has been partially decomposed, but which retains enough alkali silicate to render the mass fusible. It is quarried at St. Stephen's in Cornwall.

In Sweden felspar occurs in masses of salmon-red colour, becoming white when calcined. Pegmatite is of the same class but in a more advanced state of decomposition; it retains no mica and a very little quartz. All these are very hard and are ground in mills of special construction.

In view of the many processes of potash extraction which involve the use of lime, it is well to glance at the composition of some pottery materials. The average proportion of fusible and infusible materials is shown in the following table:—

	English China (Worcester).	Porcelain (glaze).	Sèvres (body).
SiO <sub>2</sub> .....	38.88	67.5	58.00
Al <sub>2</sub> O <sub>3</sub> .....	21.48	14.5	34.00
Fe <sub>2</sub> O <sub>3</sub> .....	—	2.5	—
CaO .....	10.06	10.0	4.5
MgO .....	—	1.0	0.5
Na <sub>2</sub> O .....	2.14	0.5	0.5
K <sub>2</sub> O .....	2.14	4.0	3.0
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> .....	20.44	—	—

Lucca della Robbia's terra cotta contained 22.4% of lime. Clays rarely contain more than 0.5% of lime, but they contain from 2% to 3.5% of alkalis. Clay is a hydrous body and when once deprived of its water can never again become plastic. Its fusibility is greater or less as its composition approaches or recedes from that of felspar. Clay containing lime is unsuitable for the manufacture of battery cells.

The best monograph on this subject is "Potash from the Natural Silicates," a paper read before the 8th International Congress of Applied Chemistry by Messrs. A. S. Cushman and G. W. Coggeshall, and published in the "Journal of Industrial and Engineering Chemistry," 1912, 4, 821. This is a summary of all the work the authors could discover, and is divided into: (1) Adaptation of natural agencies, (2) wet processes of a chemical nature, (3) dry processes in which potash salts are volatilised, (4) dry processes in which potash is separated as such or as carbonate, (5) dry processes producing the chloride, (6) dry processes producing sulphates, (7) resumé of their own large scale experiments, (8) conclusions.

The main part of their paper deals with the authors' process for treating felspar for agricultural purposes (Cushman, U.S. Pat. 987,436; this J., 1911, 488) and Coggeshall (U.S. Pat. 987,544). Cushman's process consists in powdering 100 parts of felspar with 20 parts of lime and 10—20 parts of salt. The powdered mixture is fed on to the top of a revolving drum of about 3 feet diameter in a layer about 1½ inches deep. Strong calcium chloride solution is sprinkled on this and forms calcium oxychloride, producing "clumps" in the powder. These are separated and the residue treated with calcium chloride again. The "clumps" are fed into a rotary kiln of the cement type and treated by a blast of air and powdered coal to a temperature short of that which would volatilise the potassium chloride. The product is ground and used as a fertiliser. It contains 6% of potash. It will be observed that this process evades the extraction of the potash and the utilisation of the residual clay.

In a paper read before a recent meeting of the American Institute of Chemical Engineers (see this J., 1915, p. 79) Messrs. Cushman and Coggeshall give further particulars of their process and claim that the salts obtained therefrom are at least as good as crude Stassfurt salts. They also furnish an estimate of working costs, which shows a profit without taking into account the residue. This, owing to the volatilisation of ferric chloride, is free from iron and pure white in colour, and ought to find an outlet in the manufacture of pottery, glazes, and high-class cement.

Rhodin (this J., 1901, 439) mixes 40 parts of slaked lime, 40 parts of salt, and 100 parts of powdered felspar and submits it to a temperature of 900° C., when 80—90% of the potash is converted into potassium chloride. At this temperature, little change is made in the appearance of the felspar; the lime scarcely acts on it and the salt is hardly evaporated at all. The residue is used for glass making, requiring addition of soda and silica. Given a careful control of the furnaces, the above proportions give the best results.

Herstein (J. Ind. Eng. Chem., 1911, 3, 426) proposes to heat finely powdered felspar with calcium chloride and some limestone, forming potassium chloride, and a residue available for the manufacture of cement.

A recent German Patent (Chem. Fabr. Rhenania, this J., 1912, 1179) proposes to treat phonolite with basic calcium nitrate and boil in alkaline solution under pressure (4—10 atmospheres) during 10—20 hours. It is stated that 1 ton gives 180 kilos of saltpetre. There are many other lime processes, but the above will suffice as examples.

As an example of processes in which fluorine takes part may be cited Ward and Wynant's process (Eng. Pat. 3185 of 1857, this J., 1914, 1007). Finely ground felspar is mixed with finely-ground fluorspar equivalent to the alkali in the felspar. Chalk and lime are mixed with this so that 2 parts of lime are present for one of silica, and 1½ parts to 1 of alumina and 10% excess. The mixture is heated to a yellowish-red heat for a few hours, and the porous frit so obtained is leached with boiling water. This is said to extract 90% of the potash originally present. Cushman and Hubbard in criticising Cushman's and Swayze's processes (this J., 1907, 608, 1908, and 1908, 560) state that this class of process cannot be a commercial success since the fluorine cannot be recovered owing to the excess of the lime necessary.

Another type of process extracted alum from felspar, but these were all early processes, when potash alum held the field.

In many of the fusion processes, so high a temperature was employed that potash was volatilised. Cameron (this J., 1913, 976) states that when felspar is used as a cement material, potash is found in the flue-dust.

In discussion on another paper, C. L. Parsons states (this J., 1912, 332) that cement kiln dust contains 35% of alkalis of which one-half is potash. This is worth examining. A sample of flue dust from an iron works in the Midlands was found by the Government Laboratory to contain nearly 6% of K<sub>2</sub>O, about one-third of which was directly soluble in water. Such a dust might be used locally as a manure. (J. Bd. of Agric., 1915, 1043.)

A. H. Cowles (J. Ind. Eng. Chem., 1913, 331) grinds rock phosphate with felspar in the proportion of two molecules of lime to each molecule of silica, and heats to a sintering temperature of about 1000° C. He leaches the resulting product with sulphuric acid or hydrochloric acid, obtaining either potash alum or the double chloride, phosphoric acid, and dicalcium silicate.

The Spar Chemical Co., Baltimore, Md., has done some experimental work on silicate rocks at Curtis Bay, using Thompson's process (U.S. Pat. 995,105 of 1911; this J., 1911, 955). The yield of potash is said to be 80% or 90%. For the best results the temperature must be controlled in rather narrow limits. (W. C. Phalen, Min. Res. of U.S.A., 1913, Part II., pp. 85—107.)

Another process which is worth investigation is to mix enough Redonda phosphate with felspar to replace the potash by alumina, and fuse with a large excess of salt at a temperature just below that at which salt volatilises and with just enough lime to flocculate the clay formed. The melted salt would probably contain the potash as phosphate. The residue should be available for porcelain making. The bulk of the melted salt could be poured off and used again until enough potassium phosphate accumulated in it. Fine division of the materials is essential.

A possible process (Newton, Eng. Pats. 1211 and 2421 of 1854) is to mix ground felspar with lime and soda, heap it on a hard floor, and keep it wetted and exposed to the air for a month. The drainage will be rich in potash.

Richardson (J. Ind. Eng. Chem., 1911, 3, 880) says that all the processes to deal with felspar such as fusion with salt or salt and lime, or electrolysis, give no promise of profitable working. The only hope lies in the soluble sources of supply.

In regard to direct use in agriculture, although felspar disintegrates better on weathering, mica gives better results in pot cultures and yields up potash (this J., 1912, 1088). Plants can avail themselves of about 17% of the potash in mica, 25% of that in nepheline, but less than 5% from orthoclase (this J., 1909, 722).



Phonolite meal (a mixture of "sanidine" and nepheline) has been suggested (this J., 1910, 581) as a fertiliser. It contains 9% of potash of which 3% is soluble in hydrochloric acid. Varying opinions as to its value are expressed.

Bulletin 53 (1913), U.S. Bureau of Mines, contains an exhaustive report on the mining and treatment of feldspar and kaolin by A. S. Watts.

#### *Alum.*

Potash-alum is found in the Silurian aluminoschists of Sweden, Norway, and Scotland, the coal formations (Hurlet and Campsie) in Scotland, and the lias near Whitby. All the available deposits are worked out.

#### *Alunite.*

Alunite, a hydrated basic aluminium potassium sulphate,  $KAl_3(SO_4)_2(OH)_6$ , is found in Europe in the Lipari Islands, Auvergne, and the island of Milo. When pure it contains 11% of potash. On powdering and ignition most of the potassium sulphate leaches out, leaving alumina behind. Seven miles S.W. of Mary's Vale, Utah, it occurs in a large banded vein, cutting the volcanic rock at steep inclination. The solid alunite is from 6 to 20 feet thick, and contains from 9.7% to 10.5% of potash. Assuming an average width of 10 feet in the principal vein for a length of 3,500 feet, this gives a surface area of proved outcrop of 35,000 sq. ft.

Calculating this alunite at 175 lb. per cub. ft., there would be approximately 300,000 short tons of the rock, or 30,000 tons of potash for each 100 feet in depth. (U.S. Geol. Survey, Bull. 511.)

A deposit of it, called locally "Galafatite," has been discovered near Benahabux, 6 miles from Almeria, Spain (this J., 1911, 282). Concessions have been granted over 2470 acres, and it was reported that the mineral would be placed on the market at once. Ignited alunite makes a good fertiliser.

#### *Leucite.*

Leucite occurs imbedded in volcanic rocks. No deposits in Great Britain are recorded. It is abundant in the lavas of Vesuvius, the tufas near Rome, and the "peperino" of Albano. The Leucite Hill, Wyoming, contains more potash than any other igneous rock. Eight analyses of "Wyomingite" and "Oreinite" from this region show an average potash content of 11%. An available supply of 197,000,000 tons of potash from this source is estimated. (U.S. Geol. Survey, Bull. 521.) Its composition is  $Al_2O_3 \cdot 3SiO_2 + K_2O \cdot SiO_2$ . It is soluble in hydrochloric acid without gelatinising.

#### *Waste liquors of cellulose pulp mills.*

Seidel (this J., 1898, 178) thus describes the constitution of waste liquors from the sulphite pulp process: liquor of Silesian Mill working the Ritter-Kellner process: sp. gr. 1.050; total solid residue (dry at 100° C.) 12.013 grms. per 100 c.c., i.e., 11.44% containing 9.54% total sulphur, 93% of which exists as organic compound. Potash amounted to 1 grm. in 52 litres.

J. F. Briggs states that the soda lyes used in the boiling of esparto are all evaporated and incinerated for the recovery of 85—90% of the original soda. These lyes contain only traces of potash as the ash constituents of the plant are practically resistant to the comparatively mild digestion. The potash accumulated after indefinite re-utilisation of the soda never exceeds 1—2% of the total alkali. If this lye were fused with feldspar, there would still be the problem of separating the potassium silicate from the large excess of sodium silicate. Thus no potash is to be expected from cellulose liquors.

#### *Sugar residues.*

A great deal of potash has been recovered from beetroot residues, but this cannot be regarded as a source of potash for general use, as no continuous crops of beetroot can be grown unless the potash goes back to the soil. In a review of the results of 1890 (this J., 1891, 282) a serious reduction in the French production is mentioned, and 24,000,000 kilos. of potash are said to have been refined during the year.

Potash was recovered at one time from syrups by the Duncan and Newlands process (this J., 1883, 319). When as much sugar as possible had been crystallised out, aluminium sulphate and sulphuric acid were added and the alum so produced crystallised out. Mr. W. B. Clark of Greenock states that, so far as he knows, that process is no longer worked in any refinery. No potash is being recovered in any of the Greenock refineries. The molasses containing the raw sugars are worked away in the form of yellow sugars and golden syrups. Unless the molasses were separated and afterwards fermented and the residues ignited no potash could be expected from this source. Moreover, says Mr. Robt. R. Lyle, an exhausted residual molasses, which is periodically turned out, goes out of the town to the distillers or for cattle feeding and its quantity is small. At the present time the refineries are obtaining their raw products from cane sources and it is generally accepted that the potash content of the residual molasses therefrom is lower than in a molasses from beet. Practically there is now no potash available from this source.

#### *Potash from wool scouring.*

At Field Head Mills, Bradford, the greasy raw wool, containing 40—50% of grease and dirt and about 4% of potash, is washed in two series of bowls, consisting of four bowls each. It is then carded and goes through two bowls of soap solution to remove oil and dirt. The suds from the wash-bowls are treated by the Smith-Leach process, in which pure wool-grease is extracted centrifugally, the water evaporated, condensed and used again. The potash is also recovered and used again for scouring (this J., 1903, 851—852).

Bott (this J., 1883, 123) states that 1000 lb. of wool yields 90 lb. of potassium carbonate and 5—6 lb. of other potassium salts. The quantity of wool washed in a certain district in France amounted at one time to 30,000,000 kilos. a year. This would give 1,200,000 kilos. of potassium carbonate worth £85,000. In 1890 the French production had dropped to 4,000,000 kilos.

Prof. Gardner, of the Technical College, Bradford, writes that as nearly as he can ascertain, the annual production of wool grease in Bradford is about 5500 tons. On the average 100 lb. of raw wool yields 18—20 lb. of grease and the amount of potash naturally accompanying this is 5—6 lb. Successful potash recovery plants were in operation until about ten years ago. Owing to trade conditions, however, the process is no longer profitable. The wool now scoured in Bradford is practically all blends of sheared, skin and slip wool, and it is found impossible, even by a reverse flow process, to obtain the potassium salts in more than 4% solution. In France, says Prof. Gardner, the wool treated is nearly all greasy "B.A." wool which gives about 13% solution, and the difference in cost of evaporation of the two solutions is sufficient to make the process practicable in one case and not in the other.

In conclusion, the "Reports of the Juries," International Exhibition of 1862, contain under Class II., Section A., pp. 41—57, a most interesting monograph on "Potassium Compounds," by the late A. W. von Hofmann, F.R.S., who acted as Reporter to the Section.

## DISCUSSION.

Mr. ALEX. E. TUCKER said that, notwithstanding the wide distribution of granite, on the weathering of which the formation of china clay depended, china clay was of less frequent occurrence than might be expected. He had found that finely divided felspar obtained from such weathered granite gave a distinctly alkaline reaction on simply agitating it with water, and that when carbon dioxide was passed into the water, the extraction of potash was much increased, and potassium carbonate seemed to be continuously formed over a considerable period. The same result was obtained with powdered mica and other alkali-bearing minerals found in such weathered granite. On repeating these tests with powdered orthoclase, containing some 12% of potash but which did not appear to have been weathered at all, a total extraction of only some 0.4% of alkali could be obtained with water and even with strong acids with or without digestion under pressure, etc. It therefore seemed to follow that although some wet processes might be successfully adopted for the extraction of potash contained in such minerals, regard must be had to their physical condition, and it would appear that the fritting processes described by Mr. Cresswell would be likely to give the best results.

Dr. R. S. MORRELL said that farmers were not utilising the potash obtained from wood ashes, and that valuable source of supply was unfortunately not fully appreciated by them. It seemed probable that as kainit was dear its use this year might be foregone. It had been stated (University Coll. of N. Wales, Bangor, Dept. of Agric.) that the application of common salt to the soil would increase the proportion of potash available by acting on unavailable supplies.

Mr. F. R. O'SHAUGHNESSY, in reply to a question, said that no potash could be expected from sewage. The percentage was very small and the dilution very great.

Mr. CRESSWELL, in reply to a question from the Chairman, said that Rhodin and Cushman and Coggeshall had given some estimate of cost. Most of the sources mentioned would be dearer than Stassfurt salts; how much dearer would depend on local circumstances.

asserting the presence of nitrate on the evidence of the "black-ring" test alone, and tests of the order of delicacy of the diphenylamine reaction are, for many purposes, too sensitive. An over-sensitive reaction may mislead the analyst; when such an one is used it becomes impossible to distinguish between a slight contamination and a deliberate admixture.

Tests involving the reduction of nitrates to ammonia are necessarily slow, and are not easy of qualitative application when ammonium salts are present.

The author required a test for nitrates which should be of the same order of delicacy as the "black-ring" test, easy and quick in manipulation, and of very general applicability. Such a test was suggested by the well-known action of sulphonated salicylic acid on nitrates, used in the quantitative determination of total nitrogen in fertilisers containing nitrates. Nitrosalicylic acids are produced when salicylic acid is dissolved in sulphuric acid and the mixture is heated with a nitrate. These, like the nitrophenols, are pale-coloured, but give intensely yellow (or red-yellow) salts on the addition of an alkali. It is on the foregoing reactions that the present test is based.

*Method of manipulation.*—Two grms. of salicylic acid is dissolved in 30 c.c. of sulphuric acid (sp. gr. 1.84). The test is applied as follows:—If the substance to be tested is a solid, it is cautiously heated in a test tube with a slight excess of the reagent. A drop of the resulting liquid is withdrawn on to a cold white porcelain slab and two or more drops of concentrated potassium hydroxide solution are added—enough to make the drop alkaline. The development of a yellow or orange colour indicates the presence of nitrate.

If the substance to be tested is in solution, two or three drops are placed in an evaporating dish, casserole, or porcelain crucible, two or three drops of the reagent are added and the mixture is warmed cautiously over a Bunsen flame till acid fumes are evolved. When cool, a slight excess of potassium hydroxide is added, as directed above. A distinct yellow colour is given by one drop of a 0.1% solution of potassium nitrate.

Strong aqueous ammonia may be substituted for potassium hydroxide solution, but the yellow colour produced is more fugitive.

The presence of halides does not interfere with this test.

The author wishes to express his indebtedness to Professor J. Bishop Tingle for kindly submitting this reaction to the test of use by students. Report of the result of these trials is so favourable as to make it seem worth while to publish this note.

## Canadian Section.

Meeting held at Toronto, on Friday, 26th February, 1915.

PROF. J. WATSON BAIN IN THE CHAIR.

## A QUALITATIVE REACTION FOR THE DETECTION OF NITRATES.

BY ALFRED TINGLE.

The author has frequently felt the need of a readily applied reaction for nitrates which would serve as a substitute for, or check upon, the well-known "black-ring" and "red fume" tests. It sometimes happens that one or both of these is inapplicable to the substance under examination. For instance, a meat preservative containing much sodium hydrogen sulphite and a small amount of potassium nitrate might well fail to give "red fumes" with sulphuric acid and copper; yet a cautious analyst would hesitate before

## Liverpool Section.

Meeting held at The University, on Wednesday, February 17th, 1915.

MR. FRANK TATE IN THE CHAIR.

## THE CONSTITUTION OF ORGANIC COMPOUNDS IN RELATION TO THEIR ABSORPTION OF LIGHT.

BY PROF. E. C. C. BALY, F.R.S.

There have been published during the last few years a number of papers which deal with the

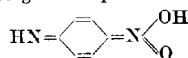
absorption spectra of organic compounds and which attempt to determine the constitution of these compounds from the shape of the absorption curve. All such attempts are based on the primary assumption that there exists a definite correlation between the constitution of a compound and the power which it exerts of absorbing light. All these light observations have dealt with the ultra-violet and visible regions of the spectrum, no reference whatever having been made to the absorption of light in the infra-red region. This is somewhat surprising, for many compounds have been investigated as to their power of absorbing infra-red light, and it also must be remembered that this spectral region is very extensive, being about 500 times as long as the ultra-violet and visible regions combined. It would seem obvious that there must be an intimate connection between all the absorption bands exerted by a compound, in whatever region of the spectrum they may occur, and yet, in spite of this, all the attempts that have been made to correlate light absorption and structure have been based on observations made in the ultra-violet and visible regions.

One of the oldest theories which attempts to correlate absorption and structure is that known as the quinonoid theory. From a general and casual survey of coloured compounds, especially of the dyestuffs, it certainly appears as if the quinonoid theory were justified by the facts. When, however, the problem is investigated more closely, the issue is not so clear as might at first be thought. As long as the physiological sensation of colour is adopted as the criterion, the difficulties connected with the theory are not very prominent. It is true that highly coloured compounds, such as diacetyl,  $\text{CH}_3\text{COCOCH}_3$ , do exist for which a quinonoid structure seems to be inadmissible, yet the main fact remains that by far the greater majority of coloured compounds belong to the aromatic series, where the quinonoid configuration can be made use of. It is when the coloured compounds themselves are scientifically investigated that the real difficulty of the problem is encountered. Two substances may well appear of identical colour to the eye and yet be entirely different in their powers of absorbing light, and hence it is impossible to accept ocular evidence in this respect. Therefore a scientific basis must be found to which the light absorption can be referred, and the most obvious one is the measure of the amount of light of different wave-lengths which is absorbed by a definite molecular concentration of the compound in question. It is most satisfactory to express all such observations in terms of a normal solution, and in Fig. 1 is shown a typical absorption curve, which represents the amount of light absorbed by a normal solution of phenol in alcohol. On the ordinate is placed the molecular absorptive power in terms of the

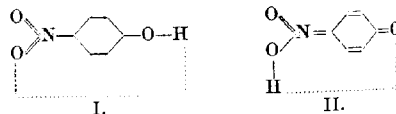
molecular extinctions, that is to say  $\log \frac{I_0}{I} \times \frac{1}{Cd}$ ,

where  $I_0$  is the intensity of the light incident on the solution,  $I$  is the intensity of the light after it has passed through the solution,  $C$  is the concentration expressed in terms of the number of gram-molecules per litre, and  $d$  the thickness of the solution in cms. The curve therefore shows the absorptive power exerted by 1 cm. of a normal solution for light of various wave-lengths. As may be seen, phenol shows an absorption band with its centre at about  $\lambda = 2720$  Angströms. Now when the absorption curves of many substances are examined, it is very often found, as foreshadowed above, that two compounds apparently identical in colour show entirely different absorption curves. Clearly, therefore, colour alone cannot be accepted as a criterion, and it becomes necessary to attribute

each absorption curve to a definite molecular structure if it still be desired to uphold the doctrine of colour-structure correlation. When, however, the absorption curves of compounds are systematically investigated, it very soon becomes apparent that the quinonoid theory is by no means as secure on its foundations as was supposed. Two difficulties at once make themselves apparent. In the first place it is found that by far the greater number of compounds exhibit absorption bands. Some of these absorption bands lie in the ultra-violet and some in the visible region. These bands may, indeed, appear in any position in the ultra-violet or visible. It may well be asked at what position in the spectrum must an absorption band lie in order for it to be accepted as evidence of a quinonoid structure. In the second place there are several highly coloured compounds for which quinonoid structures seem to be impossible. Thus nitronaphthalene is bright yellow, acenaphthylene is red, and in neither case is a quinonoid formula obvious. Then again, although *o*- and *p*-nitroaniline may be given a quinonoid structure, e.g.,

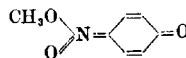


the corresponding nitrodimethylanilines cannot have an exactly analogous quinonoid constitution. The absorption curves of the parent compounds and their dimethyl derivatives are, however, practically identical, as may be seen from curves I. and II. on Fig. 3. These and similar difficulties have fully been recognised by Hantzsch, to whom we owe much for his exhaustive spectroscopic examination of numerous organic compounds. Fully recognising the difficulties in the way of the quinonoid theory as generally formulated, Hantzsch has extended the theory and has introduced the conception of "valency isomerism." The essential novelty about this idea lies in the use of the secondary valencies rather more definitely than was done previously. For instance Hantzsch puts forward two different formulae for *p*-nitrophenol:—

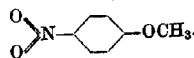


the dotted lines showing the play of forces due to the secondary valencies. Of these he says I. is colourless and II. is coloured, and on this view the coloured alkali salts would be derived from form II.

The quinonoid theory receives some support from the discovery by Hantzsch and Gorke of the existence of highly coloured ethers of certain nitrophenols. These substances are very reactive and very unstable, and they pass over with great ease into the ordinary and well-known colourless ethers. Hantzsch and Gorke\* proved that these highly coloured substances are isomeric with the ordinary forms of the ethers, and they considered it to be in the highest degree probable that they possess a quinonoid structure. They assumed that, in the case of *p*-nitrophenol, the highly coloured ether would have the formula,



and that this compound passes over with great readiness into the ordinary form,

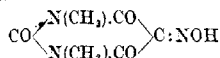


\* Ber., 1906, 33, 1073.

It would seem, at first sight, that this work afforded a direct support to the quinonoid theory, and indeed it is mainly on these results that Hantzsch has based the whole of his theories of the structure of compounds in relation to their absorption.

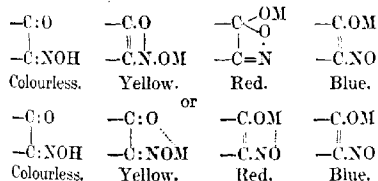
The problem became somewhat more complex when Hantzsch discovered that more than one coloured salt can be obtained from a single colourless acid. Such examples are especially noteworthy in the case of violuric acid and its dimethyl and diphenyl derivatives. From these acids colourless, yellow, green, orange, red, violet, and blue salts may be obtained, all of them isomeric and monomolecular.\*†

From the point of view of the quinonoid theory these differently coloured salts are peculiarly interesting, because it does not seem to be an easy matter to write a quinonoid formula for dimethylvioluric acid



and yet the acid is colourless and its salts coloured.

Now Hantzsch in all his work has started from the categorical statement that every appearance of colour or change of colour on salt formation is due to intramolecular isomerisation. Further he says that each isomer is characterised by a definite type of absorption curve. According to these tenets it is necessary to devise a different structural formula for each of the differently coloured isomers. As regards the violurates Hantzsch begins by saying that there are only four definite isomeric modifications, colourless, yellow, red, and blue respectively. The orange, green, and violet salts he says are mixtures. He points out that the isomerisation in all probability is only concerned with the oximido group and the neighbouring carbonyl group. Hantzsch gives two alternative sets of formulae, in which M stands for a colourless monovalent metallic atom.



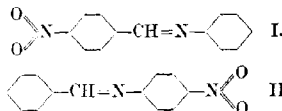
Apart from any other question, it is somewhat difficult of acceptance that two differently coloured modifications of the same molecule should exist, in one of which the secondary valencies are active and in the other they are latent. If secondary valencies are playing a part, then surely they must be considered to be of essential importance in every salt.

Hantzsch has made use of structural formulae very similar to the above in explaining the differently coloured derivatives from several colourless parent compounds. There is no need specifically to mention other instances beyond those given above, which are sufficient to illustrate the position taken up by Hantzsch. There is, however, one other phenomenon which Hantzsch has dealt with, and that is the existence of more than one modification of the same coloured isomer. This introduces a new complexity into the problem. A good example of this new phenomenon is afforded by *o*-tolyl-2,4-dinitroaniline, which can exist in four modifications, two of which are orange and two yellow. Hantzsch calls the two types of isomers chromoisomers, namely those which differ

in colour, and homochromoisomers, namely those which have the same colour. He attributes the latter entirely to stereochemical differences, but in spite of all endeavour he finds that the total number of isomers in several cases is greater than the structural theory can explain.

It will be seen from the above that Hantzsch has made considerable advances beyond the older quinonoid theory. He views the quinonoid conception as one special case of his theory. It may, however, be pointed out that there is no real basis for any one of his conclusions. There is not one single particle of scientific evidence to show why any one of his structural formulae should exhibit a colour different from any other. The mere fact that different molecular structures can be drawn is no explanation of the fact that differently coloured forms exist. Then, again, there is the added difficulty arising from the fact that there are more coloured modifications than possible structural formulae in many cases, for it must not be forgotten that in the violurates three differently coloured modifications were dismissed as being mixtures of other forms.

In these laboratories there have been made a number of investigations into the absorption spectra of organic compounds, and the general result of these is that the Hantzsch theory is entirely untenable. In fact the evidence is very strongly against there being any direct correlation between absorption and primary structure. Inasmuch as such correlation is the fundamental principle of the quinonoid theory, so the results must also be considered as antagonistic to this theory. Apart from there being no scientific basis for such correlation, that is to say there is no physical reason why a quinonoid structure should selectively absorb visible light more than invisible light, many facts have been noted which are in direct opposition to it. Three compounds have already been quoted which are coloured and yet without a quinonoid structure, diacetyl,  $\alpha$ - and  $\beta$ -nitronaphthalenes, and acenaphthylene. To these may be added azobenzene and dimethylamino-azobenzene, both of which are highly coloured and yet no quinonoid structure is possible for either of them. Then again the two sets of isomers, the nitrobenzylidene-anilines and the benzylidene-nitroanilines form a striking example



When the nitro group is substituted in the benzene residue (I.) a simple quinonoid formula is possible, but in the isomeric compound (II.) this is not the case. The absorption spectra of all these compounds are strikingly similar, there being, however, more marked absorption bands in the case of the compounds (II.), that is to say those compounds which can exist in the quinonoid form show less marked absorption than those which cannot do so.\* It is clear, therefore, that the quinonoid theory entirely fails to explain the colour and absorption of these compounds. Many other instances might be quoted of cases which are at variance with the quinonoid theory, but sufficient has been said to justify the statement that this theory not only entirely fails to give a scientific explanation of the selective absorption of light, but it also is quite inapplicable in numbers of cases where marked colour is exhibited and no quinonoid structure is feasible. Similarly Hantzsch's theory offers and can offer no explanation of the differences in absorptive power shown by isomeric compounds.

\* Hantzsch. Ber., 1909, 42, 966.

† Hantzsch and Robinson. Ber., 1910, 43, 45.

\* Baly, Tuck and Miss Marsden. Chem. Soc. Trans., 1910, 97, 571.

It is obvious that neither theory can be accepted and that the explanation is yet to be found of the origin of selective absorption in the first place and in the second of the existence of many differently coloured forms of the same compound. Any explanation, in order to be accepted, must be capable of satisfying all the chemical facts and all the variations in the absorptive power of compounds. It must also correlate the absorption throughout the whole spectrum and at the same time give a physical theory of the mechanism of selective absorption.

It is a well accepted fact that chemical atoms possess electromagnetic fields of their own, and one important proof of the existence of these fields is to be found in the Zeeman effect, which is the resolution of spectrum lines into doublets and triplets when the luminescent atoms are brought into an external magnetic field. These fields must possess a polar factor, and consequently when two atoms of different elements exist in a molecule there must ensue a condensing together of the force lines of the respective fields, with the escape of energy and the establishment of a molecular force field. It may readily be shown how the existence of these closed molecular fields is capable of explaining all the phenomena of chemical reaction and reactivity. It is not proposed in this paper to deal with this aspect of the theory, but rather to show how the theory gives a reasonable explanation of the selective absorption such as is shown by chemical compounds and also of the existence of series of differently coloured salts from colourless acids or bases. The chemical side of the theory, however, must very briefly be referred to, in order that the application to absorption phenomena may be understood.

The essential feature of the theory is that chemical reactivity may be attributed entirely to the force fields which surround all molecules. When two molecules, the force fields of which differ in type, are brought together, there will at once be formed an addition complex of the two owing to the condensing together of the force lines of the two fields. Within this complex there will naturally exist potential gradients, and if these gradients be sufficiently steep, one or more electrons will tend to pass over from one atom to the other within the molecules. If such electronic transference takes place new chemical individuals will be produced and a specific chemical reaction will have occurred. If, however, the potential gradients are not sufficiently steep, the addition complex first formed will remain as such. Although whenever two substances are mixed there will always be formed an addition complex between the molecules, no chemical reaction will take place unless the potential gradients within the complex are sufficiently steep to cause the electrons to move from one atom to another. There must obviously be a complete gradation from the condition when, owing to the force fields of the two molecules being exactly the same, no mutual influence is evidenced, to the condition when a chemical reaction occurs.

On these lines the reactivity of a molecule must depend upon its external force field. In the formation of this force field much will depend upon the force fields of the atoms composing the molecule. If these atomic fields happen to be equal and opposite the resulting molecular field will be entirely closed and such a molecule will possess no measurable reactivity when in the pure state. No doubt such cases as the want of reaction between hydrogen chloride and ammonia, when these compounds are pure and dry, are due to the fact that their force fields are entirely closed. On the other hand, it may happen that, after the maximum possible condensing together

of the atomic force lines has taken place, there is left over an uncompensated residuum. In such cases as these the molecule will possess residual affinity.

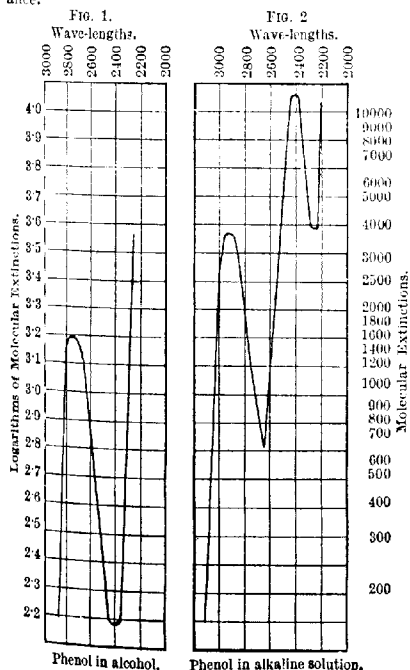
It follows from this that the reactivity of any molecule must be enhanced when its closed or partially closed field is opened or unlocked. This opening up may be produced by means either of a solvent or of light. If a substance, the molecules of which possess closed force fields, be dissolved in a solvent, the molecules of which possess residual affinity, the free force lines of the solvent molecules will interpenetrate the closed fields of the solute so that the latter are opened up and capable of reacting with any other suitable substance dissolved in the same solvent. There will be formed addition complexes between solute and solvent, usually known as solvates, and in these complexes the originally closed fields of the solute molecules will be opened up, in that some of the originally condensed force lines have been broken to reform with those of the solvent. It must clearly be understood that the condition here described is a perfectly general one and always exists when such molecular types are brought together, whether an actual solution is formed or not. Again, when such a condition obtains as described, it does not by any means follow that all the molecules of the solute have their force fields opened up. A type of equilibrium is established between the opened up molecules and the non-opened up molecules of the solute, and the reactivity of the mixture will depend upon this equilibrium.

The second method of opening up the force fields is by the action of light. Due, as they are, primarily to the rotation of the electrons, it follows that these force fields will respond to and absorb definite light vibrations. The light energy, in being absorbed, does work upon the systems and shifts the equilibrium towards the reactive side, or, in other words, it increases the relative number of opened up molecules which are present in the equilibrium. A new photodynamic equilibrium is thus established. In this way the selective absorption of light by substances is explained, for every single system in which an equilibrium exists between opened up or non-opened up force fields must be able selectively to absorb light of a definite vibration frequency.

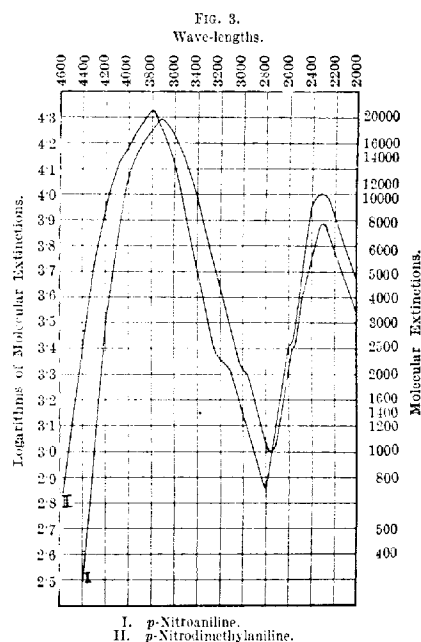
The mechanism of the opening up of a closed field may be dealt with more fully. The opening up of any given force field no doubt consists in the attacking by the solvent of one or more potential gradients. In the case of a complex molecule, the force field itself will also be complex and will contain many potential gradients. As these in turn are attacked, so it is to be expected that the action of solvents on such a complex field would be progressive. It follows, therefore, that the opening up takes place in definite stages, each stage marking the resolution of one particular gradient. Now each stage must necessarily possess a power of selectively absorbing light rays, and the various stages in the opening up of a given complex field will be capable of recognition by the vibration frequencies of the light which they selectively absorb. These stages may be called into play by the use of suitable solvents, and thus it follows that from one given complex primary structure it is possible, by the use of suitable solvents, to call into play different stages in the opening up of the molecular force field. Each of these will exert different absorptive powers, each will show its own absorption band, and the higher the stage in the opening up the longer the wave-length of the light absorbed. If these absorption bands happen to be in the visible region the different stages will have different colours. There is, therefore, absolutely no necessity to postulate any change in primary structure to account for variation in absorption.

for the whole is due to changes in the condition of the force field which is an attribute of one single unaltered primary structure.

In general, the more complex the force field the greater the number of possible stages and therefore the greater the number of absorption bands to be shown. Such cases frequently occur in organic chemistry where all the molecules are relatively complex. Before applying the theory to specific cases two points may be dealt with. In the first place, it is obvious that the most appropriate solvent to open up a force field will be one the residual affinity of which is opposite in type. For example, the force field of an acid will most readily be opened by a basic solvent and *vice versa*. Then, again, the force field may be of such a nature that it is opened both by a basic and an acid solvent; in such a case the mechanism of opening up will be different and the solute force field will be amphoteric. Further, in the case of a complex force field, the stage in the opening up called into play will depend upon the difference between that field and the residual affinity of the solvent. Thus, with a complex acid, the more basic the solvent the higher the stage in the opening up that will be called into play and the longer the wave-length of the light that is selectively absorbed. In the second place, the condition existing in the addition complex must be considered. When the force field of an acid, for example, is opened up by an alkaline solvent, an addition complex of the two will be formed. The condition of the force field of the acid in this addition complex will entirely depend upon the potential gradients set up. The force field may remain opened or it may give a new closed field, according to the steepness of the gradients. The essential conclusion follows that, in the event of a coloured salt being formed from a colourless acid and colourless metal, the colour and absorption band of the salt are due to the acid force field and to this alone, and the fact that a salt may be formed is of secondary importance.



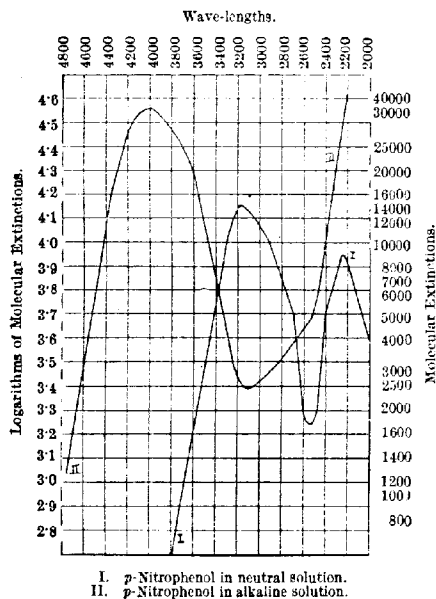
The theory may now be applied to certain specific cases in order to show how far simpler is the interpretation of colour and absorption compared with that based on the old colour-absorption correlation theory. As first examples the nitrophenols and the nitroanilines may be taken. In Fig. 1 is shown the absorption curve of phenol in alcoholic solution and it shows an absorption band, that is to say the force field of phenol is opened up by the residual affinity of the alcohol to one stage which is characterised by its power of selective absorption of light of a wave-length of about 2720. If now sodium ethoxide be added to the solution the absorption is changed considerably. Phenol is an acid substance and consequently its force field will most easily be opened up by a basic solvent. In the presence of alkali the force field is opened to a higher stage than in neutral solution, for the solution now selectively absorbs light of wave-length of about 2900. There is also present some of a stage lower than that present in neutral solution. The absorption curve of the alkaline solution is shown in Fig. 2, and the existence of the two absorption bands, proving the presence of two stages, is well shown. Altogether, therefore, three stages in the opening up of the force field of phenol have been realised with powers of absorbing light of approximate wave-lengths 2900, 2720, and 2400 Angströms respectively. Of these the first and third are called into play in alkaline alcoholic solution and the second in neutral solution.



Exactly analogous results are obtained with all the three nitrophenols, for all three isomers exhibit absorption bands in neutral alcoholic solution which evidence the existence of definite stages in the opening up of their force fields. In the presence of alkali higher stages in the opening up are called into play, proved by the presence of absorption bands of lower frequencies. These new bands happen to be in the visible region of the spectrum and therefore the alkaline solutions are visibly coloured. Now the absorption curves of the alkaline solutions are similar

in one respect to those of the corresponding nitroanilines and nitrodimethylanilines. In the latter compounds alcohol alone is capable of calling into play analogous stages in the opening up of the force fields, so that the frequencies of their absorption bands are not far removed from those of the absorption bands shown by the alkaline solutions of the nitrophenols. The essential deduction from the present theory is that each absorption band is to be interpreted as evidence of one stage in the opening up of the force field of one single primary structure. Each nitrophenol in alkaline solution is very similar to the corresponding nitroaniline and nitrodimethylaniline in neutral solution. Analogous stages are called into play, and each stage is a function of one single primary structure in each case. This explanation at once removes the difficulty connected with the nitrodimethylanilines on the quinonoid theory, for these compounds, although they closely resemble their parent bases in absorption, cannot possess a quinonoid structure. A further difficulty also vanishes, for it is somewhat of a strain on chemical formulae to picture a quinonoid structure for sodium *m*-nitrophenoxide, *m*-nitroaniline, and *m*-nitrodimethylaniline. The absorption curves of these compounds, however, bear exactly the same relation to one another as do the curves given by the ortho and by the para isomers. It is, indeed, impossible to believe that any change of structure takes place when the three nitrophenols are converted into their salts, and the present theory fully explains the variation in the absorption which takes place as being due to changes in the molecular force fields. There is no doubt that the constitution of each compound is that determined by chemical means, namely  $C_6H_4(NO_2)(OX)$ ,  $C_6H_4(NO_2)(NH_2)$ , and  $C_6H_4(NO_2)(NCH_3)_2$  respectively, where X stands for hydrogen or a colourless metallic atom. The absorption curves of *p*-nitrophenol, *p*-nitroaniline, and *p*-nitrodimethylaniline are shown in Figs. 3 and 4.

FIG. 4.



Perhaps the most striking case is that of the various coloured salts of diphenylviolic acid

prepared by Hantzsch and Robison.\* Now the force field of this and analogous acids will naturally be opened by alkalis, and owing to the complexity of the molecule many stages will exist. The particular stage called into play will depend upon the strength or electropositivity of the alkali used; the stronger this is the higher the stage that will become active. The series of alkali metals, Li, Na, K, Rb, and Cs, increase in electropositivity with increase in atomic weight, and thus it is not surprising that the stages induced by these metals differ. It must be remembered that the molecular structures, and hence the force fields of these acids, are much more complex than those of the nitrophenols. Up to the present it has not proved possible to obtain different stages of the latter compounds with different metals. It is not possible to reproduce on one diagram the absorption curves of all the salts, but on Fig. 5 are shown those of diphenylviolic acid (I.) and its lithium (II.) and caesium (III.) salts as given by Hantzsch and Robison. In this diagram the old method of plotting is employed. The curves mark the limits of total absorption at the various concentrations. The free acid shows an absorption band at a frequency of 3830 and therefore one stage in the opening up is present in this case. A higher stage is called into play in the case of the salts, characterised by the absorption band with frequency of 3220. Higher stages are also called into play in the latter case, for the lithium salt shows a band at 1890, while the caesium salt shows a higher stage still at 1680. The greater electropositivity of caesium is responsible for this stage, which is higher than that induced by the less electropositive metal lithium.

Very strong confirmatory evidence of this theory is obtained in the following way. It has been shown in a previous paper† that, on the energy quantum theory, if all the absorption bands evidenced by one compound are functions of one single unaltered primary structure, there must exist a constant difference between their frequencies and further that this difference must equal the frequency of an absorption band in the infra-red region of the spectrum. This at once places the theory upon a quantitative basis, and at the same time affords a very rigid method of proof as to whether the various absorption bands shown by a compound are functions of one single primary structure and not due to any isomerisation. There is no doubt that the infra-red absorption band is a function of the primary structure as determined by chemical analysis, and therefore, if all the visible and ultra-violet absorption bands are directly connected with this band in the manner described, it is clear that they also are functions of the primary structure.

The existence of the constant frequency differences is very evident in all the compounds dealt with above, and in those cases in which the infra-red spectrum is known, there is always found an absorption band with a frequency equal to that constant difference. It is not possible here to enter into proofs of this relation, and the statement that it exists must suffice. It is evident that this relation supports in the strongest manner the present explanation of the absorption and colour of the salts from one colourless base or acid, and that the variation in absorption is due to the condition of the force field of a given molecule with a fixed primary structure.

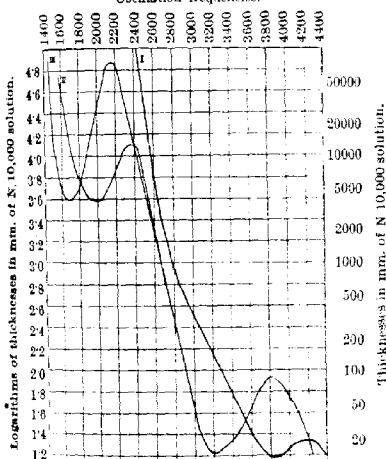
Many other instances might be given of the application of this theory, as for example the azo compounds, which form so large a branch of the dyestuffs. It seems, however, hardly necessary to do so, for every argument advanced above holds

\* Ber., 1910, 43, 45.

† Baly. Phil. Mag., 1914, 27, 632.

good in each case. The only difference between the various types of compounds lies in the type of residual affinity best designed to open the closed fields and to form the addition complexes with their characteristic absorption bands. In the case of the aminoazo compounds, for example, an acid is required since the substance is basic in type. In the case of trinitrobenzene, trinitroanisole, and picric acid, the force fields are opened to various stages by alkaline solvents, such as alcoholic sodium ethoxide, piperidine, and dimethylaniline.\* Three stages are induced in each case and the absorption curves simply differ in that the three corresponding absorption bands vary in their intensities. Another solvent which opens the fields of the trinitro compounds is a benzene solution of anthracene. In each of these solvents the opening up is due to the formation of addition complexes between solute and solvent. In certain cases these addition complexes separate in the solid phase from their solution. For example, the picrates of anthracene and other hydrocarbons are well known, as also are the addition compounds of sodium ethoxide and the trinitro compounds. The formation of these addition compounds and their colour are perfectly well explained on the present theory.

Fig. 5.  
Oscillation frequencies.



I. Diphenylvioluric acid.  
II. Lithium diphenylviolurate.  
III. Caesium diphenylviolurate.

There remains one set of observations to be discussed, namely the highly coloured nitrophenol ethers of Hantzsch and Gorke, and many similar compounds. The existence of such compounds can readily be explained by the present theory. Since a closed field is opened in stages, so the condensation of an opened up field must also take place in stages. When a nitrophenol ether, for example, is prepared from one of its salts, it must exist at the moment of formation in an opened up condition. There is no obvious necessity that, provided suitable precautions are taken, the ether should not be maintained in the opened up condition. Such a condition would be metastable and would at once in presence of a suitable solvent undergo condensation of its force lines to give the normal stable modification. Owing to the fact that the force fields are open, such metastable substances would possess abnormal reactivity

and they would, in short, exhibit all the properties attributed to them by Hantzsch and Gorke. There indeed seems every reason to believe that all such unstable isomers in reality consist of the partially opened up and hence metastable modifications of the stable forms. There is no necessity to postulate any difference in primary structure for any one of these compounds, for all the properties, both chemical and physical, are far better explained by the fact that their force fields are partially opened than by any alteration in their primary structure.

In conclusion, the evidence against change of primary structure being the cause of change in absorption is overwhelmingly strong. All the absorption bands are undoubtedly due to one atomic grouping in the molecule, as is clearly proved by the relation between these bands and the band in the infra-red region, which latter is known to be a property of that atomic grouping. One advantage of the theory may perhaps be touched upon, namely, it does away with the somewhat alarming complexity which the Hantzsch doctrine of one absorption curve one structure introduces into organic chemistry.

## New York Section.

Meeting held at Rumford Hall, Chemists' Building,  
on Friday, March 19th 1915.

MR. G. W. THOMPSON IN THE CHAIR.

## THE USE OF BARIUM COMPOUNDS IN GLASS.

BY ALEXANDER SILVERMAN.

*Historical.*—In 1829 Dobereiner suggested the use of barium compounds in glass, and though his experiments were not fruitful, records show that in 1833 fairly good glasses were obtained by Baudrimont and Pelouze.\* At Valenciennes, two factories produced a glass said to have been denser, more uniform, and more easily melted than lime glass. It is likely that barium compounds entered the batch, though the manufacturers were not aware of the fact. At a factory in St. Juste sur Loire, sand, felspar, witherite, and lime were used as raw materials; at Regout's factory in Maastricht, litharge, witherite, and lime.

Window and bottle glass were made from sand, barytes, salt cake, and a little lime by Jeanne in Paris. Benrath describes an attempt in 1871 to produce alkali-barium glass of the formula  $\text{Na}_2\text{O} \cdot \text{BaO} \cdot 6\text{SiO}_2$ . The ideas were unfruitful at the time but were later found to possess value. Harcourt also realised their possible value and Schott made valuable applications.

In more recent times barium compounds have been used in the manufacture of pressed glassware in the United States. From the reticent manner in which chemists in cut glass factories discuss the matter, the writer is inclined to concede these materials considerable value.

Compared with the action of lime, barium compounds produce glass of higher specific gravity. Barium glasses have a higher index of refraction and greater brilliancy than lime glasses and closely

\* The writer is indebted to Dr. Ludwig Springer, from whose article in *Sprechsal*, 1913, much historical material was obtained. Also to the various American chemists and manufacturers, through whose generous co-operation interesting practical data are included.

\* Baly and Rice. *Chem. Soc. Trans.*, 1913, 103, 2085.



resemble the lead glasses in these respects. The specific heat of barium glasses is lower than that of lime glasses. Elasticity and toughness are also increased by barium compounds. In hardness and coefficient of expansion barium glasses are practically identical with lead glasses.

The barium silicates are more soluble in water than corresponding calcium silicates. While more heat is required to dissociate  $\text{BaCO}_3$  than  $\text{CaCO}_3$ ,  $\text{BaSiO}_3$  has a lower melting point than  $\text{CaSiO}_3$ . According to some glass makers barium should displace calcium; others think it should take the place of alkali, and still others suggest a partial substitution for each. There are glasses on the market to-day which tend to confirm all three views, a recently published analysis of one of the Jena glasses showing no alkali, but a large quantity of barium.

To replace 1 part of  $\text{CaCO}_3$  molecularly, 1.97 parts  $\text{BaCO}_3$  or 2.34 parts  $\text{BaSO}_4$  must be used. With the latter it is necessary to use a reducing agent, theoretically 2.7% carbon, in practice 4 to 7%. It is, of course, evident that the sulphate cannot be employed as a partial substitute for litharge owing to the blackening of glasses through sulphide formation. Where barium carbonate is substituted molecularly for  $\text{PbO}$ , 0.87 part is equivalent. Taking a molecular equivalent for  $\text{CaCO}_3$ , the glass would be softer than the corresponding lime glass, so it is possible to reduce sodium carbonate or to use less barium carbonate than a molecular equivalent. The normal formula,  $\text{R}_2\text{O} \cdot \text{R}'\text{O} \cdot 6\text{SiO}_2$ , is said to work, but increased silica to present melting difficulties and cause devitrification.

American experience (Sprechaal, 1911, 566) is that an imperfect glass is obtained in tank furnaces. The glass is said to be cordy and there is a tendency toward stone formation by the action of gases producing barium sulphate. A higher temperature or the addition of zinc oxide is said to overcome this difficulty.

Zsigmondy's patent for ruby glass specifies the use of 100 kilos. sand, 16 of  $\text{BaCO}_3$ , 43 kilos. of soda ash, and 12 grms. gold. The colour is said to appear in the working of the glass.

The Jena glass previously referred to contains 12%  $\text{BaO}$ . Phosphate crown S40 from the same factory 28%  $\text{BaO}$  and 60%  $\text{P}_2\text{O}_5$ . Other Jena crowns contain smaller percentages of  $\text{BaO}$ .

Sprechaal (1909, 264) deprecates the use of more than 10 or 12 kilos. of barium compound per 100 kilos. of sand.

R. Hohlbaum ("Die Hohlglasfabrikation," p. 14) states that barium glasses are rarely produced in factories for fine ware, because barium carbonate is more costly than calcium carbonate, and glasses made from the former do not stand the fire as well. They cannot, therefore, be utilised for decorating with hard, resistant colours.

R. Dralle ("Die Glasfabrikation," I, p. 173) says that the coefficients of expansion of barium and lead glasses are identical. Barium serves mainly as a lead substitute. Its silicates have the advantage of remaining unaffected by products of combustion, whether reducing or oxidizing. Barium glasses can be melted in open pots and tanks. For cut glass barium glasses closely approximate lead glasses though they are naturally not quite equal.

Sprechaal (1912, p. 127) gives a formula for pure barium crystal for soft cut glass. Most opinions there given hold that lead should not be displaced beyond a certain point. Additional batches are found in Sprechaal, 1913, p. 268.

Chimney glass formulae, showing partial displacement of lead compounds by barium compounds, are given in Sprechaal (1906, p. 1082 and 1909, p. 389). Muspratt's *Chemie III.*, p. 1431,

credits Benrath with the preparation of a very useful glass according to the formula  $4\text{Na}_2\text{O} \cdot 4\text{BaO} \cdot 4\text{CaO} \cdot 36\text{SiO}_2$ , which might serve as a substitute for the lighter lead glasses.

Tschueschner ("Handbuch der Glasfabrikation," p. 103) recommends the use of barium sulphate and carbon in plate glass, displacing both calcium and sodium in part. Sprechaal, 1909, p. 739, calls attention to the high cost of barium carbonate, the greater specific gravity of barium glass and the consequent increase in freight charges on plate. The brilliancy is considered desirable, but mention is made of the greater fluidity of the glass and fear is expressed as to its weathering qualities.

For pressed ware barium glasses should prove desirable because of their easy flow (Sprechaal, 1908, p. 28; 1909, p. 39; 1912, p. 283).

The use of barium compounds in glass subsequently treated for the production of iridescence is mentioned in a number of works on decoration and treatment.

The following are a few quotations from replies to letters of inquiry sent to American chemists and manufacturers:—

"We have used the barium carbonate in a limited way for the past ten years and have substituted it for lime in ordinary soda lime silicate with considerable increase in the brilliancy of the product. In opal glass we have used it instead of lead. It makes the glass harder and stands fire in the decorating kiln better, but we have noticed a tendency to devitrify more than in the lead glass. We have noticed but little more, if any, difficulty in planing a soda-lime barium silicate than an ordinary lime glass. (I mention the above in view of the difficulty certain optical glasses are known to give the lens manufacturer.)"—An eastern manufacturer who requests that his name be withheld.

"I have found that barium carbonate will displace lead oxide in the manufacture of lead glass, but owing to the fact that all lead glass blanks are used for cutting purposes in this country and are polished with hydrofluoric acid, it is impossible to use this material in place of the lead owing to the fact that a fine brilliant polish cannot be obtained as with the lead oxide. If it were not for this peculiarity, there is not the least doubt but that the precipitated barium carbonate would be used very freely. Its use in making coloured glass is sometimes of importance, particularly in the case of pale greens obtained from uranium and copper, giving a colour that cannot be obtained with either zinc or lead."—Frederick Carder, Corning, N.Y.

"Barium carbonate can be used to replace lead oxide in giving density and high refractive index to glass, although, of course, in a lesser degree. The presence of barium oxide produces a glass more easily fusible than that with a corresponding percentage of lime but less fusible than glass with the same percentage of lead oxide. Viewed as an oxide used in connection with alkali to lessen the solubility of the glass, barium oxide is inferior to lime or lead because of its greater solubility. Commercial barium carbonate, the only compound suitable for introducing oxide into glass, usually contains about 1% barium sulphide. This is a marked disadvantage, and it is probable that the extended use of barium oxide will not be successful until improvements are made in the purification of the carbonate."—Dr. S. R. Scholes, Pittsburgh, Pa.

"I append herewith two analyses of window glass made in 1906 from a 'batch' containing barium carbonate. (A)  $\text{SiO}_2 = 72.29$ ,  $\text{BaO} = 5.31$ ,  $\text{Al}_2\text{O}_3 = 0.88$ ,  $\text{CaO} = 8.60$ ,  $\text{Na}_2\text{O} = 12.14$ ,  $\text{MgO} = 0.78\%$ ; (B)  $\text{SiO}_2 = 72.39$ ,  $\text{BaO} = 5.22$ ,  $\text{Al}_2\text{O}_3 = 0.84$ ,  $\text{CaO} = 8.55$ ,  $\text{Na}_2\text{O} = 12.25$ ,  $\text{MgO} = 0.75\%$ ."—William A. Hamor, Pittsburgh.

"The experiments here referred to were made for the purpose of determining if barium could be used advantageously in the making of window glass, our principal object being to overcome the production of lines or stresses, sometimes called 'reams,' when lading this glass into pots as used in the mechanical process of making cylinders for window glass. Also, to determine if any benefit would be derived in the way of increased tensile strength, or a reduction in strains and breakage, or the improving of other physical conditions so as to increase production. Therefore, a plant was selected, for the purpose of conducting these experiments, which operated a tank having a melting capacity of substantially 50 tons per 24 hours and holding approximately 500 tons. The barium was added in the form of carbonate and was gradually added to the batch in such proportions as to replace lime substantially molecule for molecule. Physical tests were made, and the chemical analyses are shown in the tables enclosed herewith. The physical test in the last column is the modulus of rupture in grams, and the column marked 'mm. deflection' is the distance through which the specimen travelled, or the deflection constant, before breaking. 'A' contained from 1% to 1½% of barium oxide, 'B' 1½% to 2½%, 'C' 2½% to 3½%, 'D' 3½% to 4½%, 'D-d,' 4½% to 5.35%, or the maximum quantity which we introduced. 'D-B' was a flat 5% of barium oxide with the silica content summing as in 'B' and, as will be noticed, there is considerable discrepancy in regard to the modulus of rupture between 'B' and 'D-B,' showing conclusively that doubling the amount of barium oxide more than doubled the modulus of rupture, but our deflection constant is substantially the same; this was a great surprise. The soda-silica ratio is the same. In Table I, I have taken a practically constant  $\text{SiO}_2$  value with varying ratios of  $\text{Na}_2\text{O}$ , and with varying or rather incremental increase in  $\text{BaO}$ . In Table II, the  $\text{BaO}$  is substantially constant (except in D-8, D-9) with an increasing  $\text{SiO}_2$  ratio, the  $\text{Na}_2\text{O}$  being constant or practically so.

TABLE I.

	$\text{SiO}_2$ $\text{Na}_2\text{O}$	$\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ %	$\text{BaO}$ %	$\text{CaO}$ %	$\text{Na}_2\text{O}$ %	mm. De- flection.	Modulus in grms.
A ....	4.81	1.37	0 to 1.5	11.51 10.78	13.59	0.38	18,170
B ....	5.12	1.21	2.5 to 3.5	10.5 9.9	13.18	0.38	21,530
C ....	5.40	1.19	3.5 to 4.5	9.71 9.1	12.05	0.55	29,500
D ....	5.07	1.07	4.5 to 5.0	9.37 8.30	12.00	0.46	44,720
D-B ..	5.12	1.07	5.0 to 5.35	9.1 8.30	12.79	0.43	45,470
D-d ..	5.02	1.00			12.85	0.48	52,780

TABLE II.

	$\text{SiO}_2$ $\text{Na}_2\text{O}$	$\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3$ %	$\text{BaO}$ %	$\text{CaO}$ %	$\text{Na}_2\text{O}$ %	mm. De- flection.	Modulus in grms.
D-d ..	5.02	1.09	5.35	8.30	12.85	0.58	52,780
D-1 ..	4.81					0.21	37,100
2 ..	4.06	1.13	5.27	8.38		0.45	36,890
4 ..	5.19					0.48	35,350
D-5 ..	5.03						
6 ..	5.38	1.11	5.28	8.35	12.90	0.50	52,370
7 ..	5.4				12.41	0.41	42,990
					12.73	0.43	39,150
D-8 ..	5.70		3.17		12.02	0.58	34,800
9 ..	5.70	1.17	4.25	8.31	12.71	0.45	35,250
10 ..	5.71		5.29		12.80	0.48	21,850

"The results were surprising, for these figures represent the mean of from three to five tests of each specimen. Glass conforming to 'D,' 'D-B,' 'D-d' or 'D-5' was made with from 40 to 80% less breakage from tank to box, according to the melting conditions, also the quality was greatly improved."—Robert L. Frink, Lancaster, Ohio.

"I have used barium carbonate in place of lead oxide with success, it being possible to replace all of the lead in a formula. Barium has been used largely in enamels using antimony salts in place of tin oxide. Enamels containing antimony oxide and lead oxide are usually very yellow. Replacing a certain portion of the lead with barium removes this objection. Barium used in molecular proportion to replace lead gives an enamel requiring a higher heat to form, but when formed the melting point is about the same as that of the lead enamel. Barium enamels are somewhat stiffer, and show no tendency to flow on the ware. Variation in barium content does not give same expansion and contraction as when content is changed and thus can not be used as a control. Lead enamels show a bright fine surface. Barium enamels are apt to show a slightly greasy surface, with many very slight pits. In enamels I consider it of advantage to carry 6% of  $\text{BaO}$ , using  $\text{BaCO}_3$  as origin. Barium fluoride acts like fluorspar, and I have found it of advantage to replace ½ of the fluorspar in my formulae with  $\text{BaF}_2$ . My experience would indicate that  $\text{BaCO}_3$  could replace  $\text{PbO}$  in lead glasses to some extent."—H. L. Bowers, Oshawa, Ont., Canada.

"Barium oxide is used a great deal in ceramic glazes. It has been found that up to 0.2 equivalent it imparts brilliancy and hardness to the glaze, and at the same time tends to lower the maturing temperature as compared with the action of lime. It seems to be used a good deal, especially in borosilicates. The only objection to barium compounds is their readiness to absorb sulphuric acid during the early stages of the burning. The resulting sulphate may give rise to surface summing. For this reason in many glazes it is introduced as part of the frit. Some European porcelain glazes carry as much as 0.2 equivalent of barium oxide. In glazes which tend to craze barium aggravates this difficulty."—Dr. A. V. Bleiminger, Pittsburgh.

The writer's personal experience with barium compounds has been confined to their use in opal and alabaster glasses. Here they can displace both lime and litharge, wholly or in part, depending on the nature of the batch. The advantage is in the increased whiteness which results and in reducing the tendency to strike, so common in lead glasses. Further, the glasses flow well for pressed ware and with proper correction a good metal is obtained for blowing. The advantage over lead glasses in fire-polishing has already been made apparent.

**Supply and cost.**—According to good authority,\* domestic crude barytes averaged \$3.45 per ton in 1913 and the refined product was valued at \$14.18. Very little carbonate or witherite is mined in the United States and there are apparently but two plants equipped to manufacture it from barytes. Barium carbonate can be bought in quantity at \$3.75 per 100 lb. There is then, obviously, a limited supply and the price would prove a material factor in certain branches of the glass industry. The demand for barium compounds in the paper, leather, rubber, textile, and paint industries and for the manufacture of the peroxide is not indicative of a reduction in price.

**Conclusion.**—Facts already established show the value of barium compounds in the manufacture of certain glasses. The price of the compounds prevents their economical use in other branches of

\* The production, manufacture and uses of compounds of barium, W. E. Emley and S. E. Young, Proc. Amer. Ceram. Soc., 1915

the industry, when the cost of cheaper glasses is considered. Further investigation may prove that improved quality will more than offset cost. Further development of natural resources may sufficiently reduce the price of these compounds to make their use more general. Both are worth while if one can judge from results already obtained.

## THE CAUSES OF THE OPALESCENCE OF GLASS.

BY JUDSON G. SMULL.

The manufacture of opal glass has come to be an immense industry in recent years, to say nothing of the increasing manufacture of enamels and enamel ware. The theory and processes of opalisation have been the subject of many investigations, with the result that many conflicting theories have been proposed to explain them. It is the purpose of this paper to give a general review of these investigations, together with some experiments performed by the author, in an attempt to ascertain, if possible, the true causes of opalescence.

Opal glass is used to a great extent in the manufacture of gas and electric globes, because its use has been found to be very effective in the distribution of light in space.\* It is known under the names, "alabaster," "bone glass," "Carrara"; the term "hot cast porcelain" was a trade name used as early as 1860, when it was manufactured extensively in Philadelphia and Pittsburgh. The substances used to produce opacity include the oxides of tin, zinc, aluminium, titanium, zirconium, antimony, and arsenic, calcium phosphate, barium carbonate, asbestos, kaolin, felspar, cryolite, fluorspar, and fluosilicates. The "hot cast porcelain" was made from sand, cryolite, and zinc oxide. There is apparently a wide range of substances which may be used to produce opacity; several, however, may be eliminated on account of their cost and difficulty experienced in working. The substances used most and which have been the subject of nearly all of the investigations are the aluminium compounds, such as felspar, cryolite, in combination with fluorspar, fluosilicates, and alkali fluorides. Some typical formulæ† are as follows:—

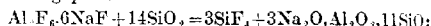
Sand .....	100	100	100	100	100
Potash .....	16		20	20	20
Soda .....		20			6
Arsenic .....	1.0	1.0		1.0	
Red lead .....	3.0	40.0	20		8
Lime .....	8.0				
Zinc oxide .....	15.0			8.0	12
Cryolite .....		22.0	20	10.0	
Fluorspar .....		19.0	20	12.0	
Felspar .....					3
Saltpetre .....					

Upon examination of these and many other formulæ, it is found in the majority of cases, that a fluoride is used with a compound of alumina, such as aluminium silicate, or again as fluo-aluminate, as in cryolite, and very seldom do we find alumina used in the uncombined form.

Opal, the mineral and precious stone found in nature, is an amorphous form of silica, transparent to opaque. It contains a varying amount of water, but the water is sometimes regarded as being non-essential. The hardness and specific gravity are lower than in quartz. The opal is formed, according to Dana's "Mineralogy," from the silicious waters of some hot springs, and often from the silicious shells of infusoria, etc., which consist essentially of opal silica. The opal is now

considered to be a solid silicic acid gel. (Zsigmondy and Siedentopf, Ann. Physik, 1913, 4, [10] 2.)

The first reference in literature goes back to 1860,\* when in Philadelphia, Pa., cryolite was used to make opal glass by the American Hot Cast Porcelain Co. In 1869, Benrath† analysed some pressed glassware of "hot cast porcelain" of sp. gr. 2.471, and found it to contain: SiO<sub>2</sub>, 67.07%; Al<sub>2</sub>O<sub>3</sub>, 10.99; Fe<sub>2</sub>O<sub>3</sub>, 1.09; CaO, trace; Na<sub>2</sub>O (calc.), 19.83%. A glass of this composition was made from 1 part cryolite and 2 to 4 parts quartz sand; the high iron content was said to come from the sand. To make a glass of similar composition, Benrath melted cryolite with sand, and found that the melt, while still molten, was perfectly transparent, and remained so until the glass cooled somewhat, when a turbidity appeared and finally, upon cooling, a dense white glass of sp. gr. 2.373 remained; the analysis compared closely with the American product. Benrath found no fluorine in this glass, and he advanced the theory that opalisation was due to the separation of crystalline alumina, and concluded that the fluorine was completely expelled from the glass as volatile SiF<sub>4</sub>. He gives the following reaction as taking place:—



In the same year, Williams‡ examined an opal glass made up as "hot cast porcelain," containing 8% F, and calculated that the approximate composition of the glass batch was: sand, 67.19; cryolite, 23.84; zinc oxide, 8.97%. He concluded that opacity was due to sodium fluosilicate, which dissolves in the molten glass at a bright heat, and passes on cooling into a porcelain-like mass, and states that the action on the pots in making this glass was no greater than in other glasses.

In 1877, Ebell§ made some investigations on opal glass, to determine the role of fluorine; on melting Benrath's mixture of 1 part cryolite and 2 parts sand for two hours at a yellowish-red heat, a great evolution and loss of SiF<sub>4</sub> was observed. A test portion taken from the melt and suddenly cooled was colourless, but on warming to the softening point the whole mass suddenly became intensely opaque. The glass which remained in the crucible cooled slowly and showed a more definite structure; it was not so dense as the former, and a thin section under the microscope showed an opaque ground mass, with a crystalline substance of wave-like appearance. An analysis of the glass showed 1.74% fluorine, and upon reheating with fine sand, a perfectly clear glass was obtained containing no fluorine. Ebell concludes that fluorine is essential in producing opacity, and that sodium silicofluoride cannot effect it without alumina.

In 1884, Johnson and Zeodesco|| (Eng. Patent 6899) made opal glass by substituting cryolite, felspar, or fluorspar for calcium phosphate, and state that the usual ingredients for an opal glass are an alkali fluoride, either with or without the conjoint use of a substance containing alumina.

In 1885, C. Weinreb¶ made a series of glasses from mixtures containing alumina and a fluoride, separately and in conjunction, from which he concluded that aluminium fluoride is formed and produces the opacity.

Schwarz,\*\* in 1888, experimented with a glass of the molecular formula, 6 SiO<sub>2</sub>, 1 PbO, 1 CaO, 1 K<sub>2</sub>O, 1 Na<sub>2</sub>O, using a mixture of three-fourths of this glass and one-fourth cryolite. He

\* This Journal, 1835, 502.

† Benrath, Dingl. Polyt. J., 192, 239.

‡ Williams, J. Franklin Inst., 57, 252.

§ Ebell, Dingl. Polyt. J., 225, 70.

|| Johnson and Zeodesco, this J., 1885, 349.

¶ Weinreb, Dingl. Polyt. Jour., 250, 361.

\*\* Schwarz, Dingl. Poly. Jour., 297, 223.

\* Schott v. Herschkovitz, J. Gasbeleucht., 1901, No. 26.

† Die Glasblüte, 37, 219, 229, 237.

contents that no fluorine is volatilised and that he experienced no bad effects from cryolite or other fluorides on the pots, provided the proper proportions of ingredients are used. Fluorine compounds in the batch up to 10% gave satisfactory results. He agrees with Williams\* that sodium fluosilicate is the cause of opacity, and that alumina plays no part in the opalisation, since fluorspar and potassium fluoride gave equally good results.

In 1898, R. Zsigmondy† made experiments from which he concluded that  $AlF_3$  is the essential constituent in producing opacity. He contended further that zinc and lead fluorides act in a similar manner, that is, they remain suspended in the glass, just as aluminium fluoride does. He also gives an example of a French opal glass, free from fluorine but high in alumina and lead, the opacity of which he attributes to lead, since in lead glass, which fuses at a low temperature, the alumina is less soluble than in those glasses not containing lead.

J. A. Reich,‡ in 1898, showed that the sodium fluoride content of cryolite was the cause of opacity, but considered that the fluorine escaped completely in the form of silicon fluoride.

K. Reidel,§ in 1909 found that, if cryolite be replaced by an equivalent amount of aluminium hydroxide, a perfectly clear glass was obtained, from which he concluded that the alumina content of cryolite alone is not the cause of opacity. Replacing cryolite by an equivalent amount of sodium fluoride and working at moderate temperatures, opalescence was produced, but not as dense as with cryolite. He also found that opalescence may be produced by using fluorspar in sufficient quantity, in the absence of all other substances used for the same purpose. Reidel refers also to an article by Tscheuschner,|| who doubted that the fluorine content of cryolite and fluorspar was essential in producing opacity.

Schaller¶ in 1909 stated that, contrary to the general opinion, fluorine does not escape completely as  $SiF_4$ , but frequently remains in the glass in considerable quantities, causing a notable change in the physical properties and at the same time producing opacity. It is further stated, however, that it should not be taken that  $SiF_4$  alone produces opacity in glass, for some observers assert that silica separates in a very finely divided condition, and is the opalizing substance. Soda-lime glasses of high silica content become opaque on cooling even without the addition of phosphate or fluoride, but the opacity may be increased by the addition of fluoride or phosphate, according to the effect desired.

Again, in 1909, Enequist\*\* concluded that opacity is caused by  $SiF_4$  in a gaseous form, as shown by the fact that "if an opal glass, particularly one containing lead, is heated to fusion it becomes clear; but, if cooled it becomes opaque. If the same or a similar piece of glass or enamel is heated as above and a part of the molten drop squeezed suddenly with a pair of tongs, the opacity will practically vanish from the pressed part."

Frank†† doubts the ability of  $SiF_4$  in gaseous form, to produce opacity; he agrees that opacity is produced by  $SiF_4$ , but considers that it remains in the glass in a crystalline form, and that it is these crystals of  $SiF_4$  that produces opacity; furthermore, the heating of such a glass

in a reducing atmosphere will break up these crystals, changing the opal glass into a clear glass.

The most recent addition to the literature of opal glass is the patent of George Macbeth, of the Macbeth Evans Glass Co. (U.S. Pat., Reissue No. 13,766, reissued July 7th, 1914). Macbeth uses the following combination as the "foundation" mixture: Sand, 100 lb.; lead oxide,  $15\frac{1}{2}$  lb.; soda,  $21\frac{1}{2}$  lb.; nitre,  $5\frac{1}{2}$  lb.; salt,  $5\frac{1}{2}$  lb.; borax,  $1\frac{1}{2}$ — $2\frac{1}{2}$  lb.; to which he adds 18-12 lb. aluminium hydroxide (containing 11-84 lb. aluminium oxide) and 6 lb. of fluorspar. The working temperature is approximately  $2700^\circ F.$  ( $1500^\circ C.$ ). The use of aluminium oxide and a fluoride, such as fluorspar, Macbeth claims "apparently produces specks, the larger of which are ordinarily visible to the naked eye, and which have the effect of diffusing or scattering the light and giving the glass its white luminous appearance. The specks in the finished ware are elongated in shape, and I believe them to be bubbles of silicon fluoride gas held in suspension in the material and elongated during pressing or blowing into moulds."

The theories of the different investigators, as to the cause of opacity, may be summarised briefly as follows: That it is produced by

- (a) Crystalline alumina, no fluorine remaining in the glass.
- (b) Sodium fluosilicate, presence of  $Al_2O_3$  necessary.
- (c) Sodium fluosilicate, presence of  $Al_2O_3$ , immaterial.
- (d) Aluminium fluoride, also by zinc and lead fluorides.
- (e) Silicon fluoride in gaseous form.
- (f) Silicon fluoride in crystalline form.
- (g) Silica in finely divided form.

#### Experimental.

The experiments to be described were carried out in a gas-fired crucible furnace; French clay crucibles were used for the fusions. A clay crucible permits of a much larger charge than a platinum crucible; the charge in each case was approximately 125 grms. Then again the influence of rapid cooling would be greatly diminished in a clay crucible charge of 100 grms. or more as compared to a platinum crucible charge of 5 or 10 grms. In fact, a clay crucible charge when compared with a charge of large scale operation presents great differences in the phenomena of glass, especially since these phenomena depend upon the production and manipulation of the glass while it is still hot. The action of fluorides on the clay crucible was not enough to produce an opal effect in any case, so that it was possible to use chemically pure substances in order to study the reactions and in all experiments where there was any doubt about the effect produced, "chemically pure" substances were used. It may be noted that no mention is made in the literature referred to concerning the use of such chemicals in any of the experimental work.

The heating in most cases lasted for two hours after complete fusion; prolonged heating was found to render an opal batch perfectly clear; the temperature of the furnace was not measured, but was estimated to be between  $1300^\circ$  and  $1500^\circ C.$  In every case the melts were allowed to cool slowly in the furnace, before breaking the crucible for examination. The batches were made up by mixing all of the ingredients together before heating, but the procedure of fusing a portion of the batch and adding the remaining ingredients after fusion appeared to be advantageous in certain cases. Small pieces of the glasses which showed opacity, became perfectly transparent

\* Williams, *loc. cit.*

† R. Zsigmondy, *Dingl. Polyt. J.*, **271**, 36, 80.

‡ Reich, *III. Int. Cong. Appl. Chem.*, Wien (1898).

§ Reich, *Chem.-Zeit.*, 1909, **33**, 1305. *Chem. Abstr.*, **4**, 512.

|| Tscheuschner, *Glas-Ind. Kalender*, 1902, 25.

¶ Schaller, *Z. Angew. Chem.*, 1909, **22**, 2309.

\*\* Enequist, *Chem. Eng.*, 1909, 54.

†† Frank, *Chem. Eng.*, 1909, 128.

when heated in the flame of a Bunsen burner, but on cooling again the original milkiness appeared.

The finished glass contained from 10–12% lead oxide, about 4–6% alumina, and about 5% lime; the silica averaged 66%, the remainder being alkalis, and possibly some fluorine. Several manufactured opal glass articles were examined and analysed. The analyses of two of these glasses are as follows:—

	Glass A.	Glass B.
	%	%
SiO <sub>2</sub> .....	65.71	66.40
Fe <sub>2</sub> O <sub>3</sub> and Al <sub>2</sub> O <sub>3</sub> .....	3.73	9.78
CaO .....	3.50	0.30
MgO .....	0.50	0.50
PbO .....	12.97	10.40
Na <sub>2</sub> O .....	12.95	12.50
K <sub>2</sub> O .....	trace	trace
MnO .....	none	none
As <sub>2</sub> O <sub>3</sub> .....	none	0.10
F .....	trace	0.85

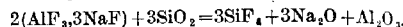
Examination of thin sections of the manufactured glasses under the microscope showed a homogeneous mass, but no crystalline structure could be detected.

In these experiments, a type of glass was chosen as previously given, and variations, either by substitution or addition, were made in the use of fluorine and aluminium compounds; the results of these tests are summarised in the following table:—

Fluorine compound used.	Aluminium compound used.	Character of glass.	Remarks.
Fluorspar, commercial.	Ignited alumina.	Very slight opacity.	Probably due to silicates in fluorspar.
Fluorspar, commercial.	Felspar	Dense, opaque	
Potassium fluoride	None	Clear	
Potassium fluoride C.P.	Ignited alumina.	Clear	
Potassium fluoride	Felspar	Opaque	
Aluminium fluoride	—	Clear	
Cryolite	—	Opaque	
Aluminium fluoride C.P.	Ignited alumina	Clear	
Cryolite (66% NaF) (40% AlF)	Ign. alumina	Slight opacity	Not as good as with natural cryolite
Sodium silico-fluoride C.P.	None	Dense, opaque	
Potass. fluoride	Sodium silicate	Opaque	
Sodium fluoride C.P.	Sodium silicate	Opaque	
None	Ign. alumina	Clear	
	China clay	Clear	
	Felspar	Clear	

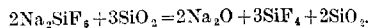
It will be seen that fluorspar and alumina produce only a very slight opalisation, while fluorspar and felspar give a dense opaque glass. Potassium or sodium fluoride may be used in place of fluorspar, giving practically the same results. Aluminium fluoride and alumina gave a perfectly clear glass. Cryolite produces opacity without the use of any silicate, as felspar, although we often find felspar in a cryolite mix. Sodium fluoride and aluminium fluoride mixed in the proportions as found in cryolite produce opacity, but not so good as natural cryolite. The results with cryolite tend to show that opalisation is not due to the separation of silica, but to the separation

of alumina, by the action of cryolite on the sand, according to the reaction:—

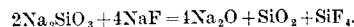


The alumina remains suspended in a low melting point glass, such as a lead glass, thus permitting a selective reaction between sodium oxide, alumina, and silica; continued heating causes the solution of alumina and renders the glass clear. Felspar, ignited alumina, or china clay heated in a glass batch, in proper proportions without a fluoride, produce a perfectly clear glass.

Passing to the silicofluorides, we find that sodium silicofluoride without any aluminium compound produces opacity. The reaction is probably as follows:—



Here the silica, like alumina, is held in suspension and here again a lead glass is best suited for the purpose. If the separation of silica takes place, as shown above, and produces opacity in the same way as alumina is thought to do, then we should expect to obtain opacity by using a silicate, free from alumina, in conjunction with some fluoride. We found this to be the case where sodium silicate and sodium fluoride were used in a lead glass batch. The reaction is expressed as follows:—



Since all natural silicates used in opal glass manufacture contain both alumina and silica in a combined form, it is probable that, under suitable conditions, there is a suspension of both these compounds in the opal glass. It is reasonable to think that in mixing an opal batch, one may first melt together the constituents which are naturally required for the glass, such as sand, soda, etc., thus forming a silicate, and to this fusion then add a fluoride and any other elements necessary. The function of the fluoride then would be to set free the silica or alumina or both, which are present in combined form, as a result of the preliminary fusion, thus producing the desired opal effect. It is possible that some of the investigators referred to may have performed their experiments in this manner, without mentioning the fact, thus obtaining results not in exact conformity with the stated facts.

#### Summary and Conclusions.

In general we say then (1) that opacity is the result of the separation of either silica or alumina or both, in a very finely divided, probably colloidal form in the glass; (2) the most suitable condition for this separation is a glass of low melting point, that is, one containing lead, where the silica and alumina will remain suspended for some time before going into solution; (3) the separation of silica and alumina is effected by (a) the use of silicates, such as felspar, in conjunction with a fluoride; (b) by a double fluoride, such as cryolite, with or without felspar; (c) by silicofluorides, with or without felspar; (d) by a fusion of the major ingredients of a glass, with the addition afterwards of a fluoride and other desired substances to the fused portion.

There is another probable explanation of the production of opacity, derived from a consideration of the refractive properties of glass with respect to the refractive properties of the oxides which appear to produce opacity. If alumina or silica or any other oxide is held in very fine suspension in the glass, then we may consider them in the same manner as we consider a pigment and a vehicle with respect to hiding power. In the case of a pigment, it is held that good hiding power is obtained when the refractive index of the pigment is materially different from the refractive

index of the oil, whilst if the refractive indices of the pigment and oil are the same there is practically no hiding power.

In the same way opal glass may be considered as consisting of a glass medium (which corresponds to the vehicle) and the very finely suspended particles (corresponding to the pigment). Then if the refractive index of the glass medium is materially different from the refractive index of the suspended particles, we shall have a good opal effect, but if the respective refractive indices are very nearly alike, we should expect to get transparency in our glass. Ordinary glass has a refractive index of 1.55, silica 1.44, alumina 1.76, and tin oxide 2.0; which means that under suitable conditions, opacity or opalescence may be produced by the suspension of alumina, silica, tin oxide, etc., in a glass medium, because of the differences in the refractive indices of these oxides with respect to the glass.

The work covered in this paper is considered only as a preliminary for further investigation, and is given in the hope of stimulating a thorough research to settle the disputed points which appear to exist. The work was carried out in the Research Laboratories of the National Lead Company under the direction of Mr. G. W. Thompson, to whom the author is indebted for many valuable suggestions.

#### DISCUSSION.

Mr. J. O. HANDY said he believed that neither alumina nor silica was precipitated as such in opal glass. The phosphate glasses doubtless contained insoluble, finely divided calcium phosphate in suspension. Glasses containing fluorides, however, he believed to owe their opacity to one or more fluorine compounds, probably siliconfluorides, which were in process of further decomposition, with production of silicon fluoride gas, which is volatilised.

With reference to the Macheth patent for a white glass free from "fire," the cause or causes of the opacity in this case seemed to be different from that of the opacity of the older types of opal glass. Photomicrographs showed the presence of numerous gas bubbles, but showed no material amount of suspended solid matter, even when a magnification of 400 diameters was used. The suspended matter in an opal glass examined microscopically could not be detected by the usual methods of microscopic examination, and bubbles were very few in number. The suspended solid matter apparently present in both glasses evidently existed in an extremely fine state of division approaching the condition ordinarily described as "colloidal."

Mr. E. ENEQUIST stated that on fusing a mixture of sand, soda, and fluorspar for a few hours, he had obtained a glass which was more opaque at the top than at the bottom, tending to show that a gas was given off, but not completely, however, since prolonged heating drove out all the gas, and rendered the glass clear. If alumina or silica were the cause of opacity, the continued heating would not cause the glass to clear, as in the case of SiF<sub>4</sub>.

Mr. SMULL replied that his experience in opal work had been that, on breaking the crucible to examine the glass, it was slightly more transparent near the top than at the centre or bottom. He believed the alumina and silica were separated in the reaction, rather suddenly, by the action of the fluorides, and that, just as prolonged heating of any glass mixture changed its constitution and characteristics, so in opal work, continued heating tended to dissolve the separated alumina and silica and render the glass clear.

*Meeting held at Rumford Hall, Chemists' Building, on Friday, January 22nd, 1915.*

MR. G. W. THOMPSON IN THE CHAIR.

#### PRESENTATION OF THE PERKIN MEDAL TO DR. EDWARD WESTON.

After some introductory remarks by the Chairman.

Prof. C. F. CHANDLER, in making the presentation of the Perkin Medal to Dr. Edward Weston, said that Weston was born at Brynm Castle, near Oswestry, in 1850, and came to America in 1870. His first engagement was with the W. H. Moduck Co., manufacturers of photographic chemicals and dealers in photographic supplies and apparatus; here he stayed about a year, and during this period and later, for about three years, he assisted Professor Charles S. Stone, Professor of Chemistry, at the Cooper Union. Then he went to the American Nickel Plating Company, where he found that the nickel plating works were in very poor condition, especially the galvanic batteries employed as a source of electricity. He carefully investigated all the details of the art, and made many improvements in the processes by which he improved the quality of the coating, secured great economy in nickel, and greatly reduced the time required for plating, and particularly succeeded in the preparation of the surface to which the nickel was to be applied and in the polishing of the nickel coating. He also discovered a dip which could be conveniently used for removing nickel from damaged goods in order to coat them again.

When this company gave up business in 1872, Weston went to the Silver Nickel Plating Company. He soon left this company, however, and was appointed consulting expert by the Commercial Printing Telegraph Company, operating the patents of Foot and Randall. This company was soon bought out by the Gold and Stock Telegraph Company.

Dr. Weston then formed a partnership with a Mr. Harris for general plating business—copper, brass, nickel, silver and gold. Here he built, in the latter part of 1872, a dynamo as a substitute for batteries in electroplating. This greatly increased his business, so he enlarged the plant and finally moved to Carter Street. Here he built another dynamo, larger and somewhat different. Then he built a third dynamo for a manufacturing firm in Newark. At this time he withdrew from the plating business and made an arrangement with the Newark firm to build dynamos for electroplating and made about twenty of them. They were so expensive, however, that they could only be used by large concerns. He started to design a simpler and cheaper machine, but the firm decided to give up the business. A new firm, Stevens, Robbins, and Hayville bought them out and Weston went into partnership in order to develop a new nickel anode which he had invented and for which he obtained his first patent in 1875.

Since then he has taken out over 350 patents for his various inventions, and has made radical improvements in several arts. Besides that, a great deal of his work has involved the most patient and careful scientific investigations, often of microscopic accuracy, and has contributed largely to the advance of scientific knowledge and theory.

In 1903, McGill University conferred upon Mr. Weston the degree of LL.D., in 1904 the Stevens Institute of Technology bestowed the degree of D.Sc., and in June, 1910, Princeton University conferred the same degree.

Dr. EDWARD WESTON, in accepting the medal, expressed his sincere thanks for the honour conferred upon him, and also acknowledged the debt of gratitude which he owed to Prof. Chandler for his kindly assistance on his arrival in New York in 1870.

Dr. L. H. BAEKELAND then spoke as follows: To the pioneer work of Dr. Edward Weston is due the development of several industries: the electro-deposition of metals, the electrolytic refining of copper, the construction of electric generators and motors, electric illumination by arc and by incandescent light, and the manufacture of electrical measuring instruments.

Weston's tendency to observe small details in chemical or physical phenomena led him to improve the art of nickel-plating and electrolytic deposition of metals to a point where it entered a new era. He succeeded in devising methods not only of increasing the physical texture of the deposit, but for improving enormously the speed and regularity with which the operations could be carried out; all these improvements are now embodied in the art of electro-plating, nickel, gold, and silver-plating.

At that time, attempts had already been made to refine copper commercially by means of the electric current. Here again, Weston established the true principles on which economic, industrial, electrolytic copper-refining could be carried out.

The whole problem of electrolytic refining, when Weston took it up, was hampered by the conception that a given horsepower could only deposit a maximum weight of copper, regardless of cathode or anode surface. Weston showed clearly how to increase the amount of copper deposited per electrical horse-power, by increasing the number and size of vats and their electrodes, connecting the vats in a combination of series and multiple, the only limit to this arrangement being the added interest of capital and depreciation on the increased cost of more vats and anodes, in relation to the cost of horse-power for driving the dynamos.

The electro-deposition of metals forced Weston into the study of the construction of dynamos. In 1876, he filed his first United States patent on rational dynamo construction, which was soon followed by many others, and before long, he had increased their gross electrical efficiency from a maximum of 40%, to 95%, and a commercial efficiency of 85 to 90%.

In Weston's factory the electric arc was used for the first time in the United States for general illumination. In fact, from 1875 to 1886, Weston was very energetically engaged with the development of both systems of arc and incandescence illumination by electricity. He started the manufacture of arc-light carbons by methods of his own invention, and thus he founded another new industry in America. Amongst the many objections to the electric arc was the bluish colour of its light. Weston found a complete remedy by the introduction of vapours of metals or metallic salts or oxides in the arc itself, so as to modify at will the colour of the light, and thus he became the inventor of the so-called "flaming arc."

In his endeavours to make the electric incandescence lamp an economic possibility, he first tried to utilise platinum and iridium and their alloys, which he fused in a specially constructed electric furnace, devised by him, antedating the furnace described by Siemens. This is probably the first electric furnace, excepting the furnace which Hare used in his laboratory in Philadelphia. But these platinum metals had serious defects apart from their high cost, and by that time Weston had become so familiar with the properties of good carbon that, like other inventors, he became convinced that the ultimate success lay in that direction.

To make carbon filaments homogeneous, Weston passed the current through them in an atmosphere of hydrocarbon gas, so that in every spot where the temperature was highest, on account of greater resistance due to irregular structure of the material, the hydrocarbon gas was dissociated and carbon was deposited automatically until the defect was cured, with the result that the filament acquired the same electric resistance over its whole length. By now Weston had become convinced that the ideal filament would be an absolutely structureless, homogeneous filament, and that such a filament could only be produced artificially from a structureless substance. He finally secured this result by evaporating a solution of collodion to produce a homogeneous, structureless, transparent film of nitro-cellulose. As this film could not be carbonised the nitrate group was eliminated by means of ammonium sulphhydrate. This gave a flexible, transparent sheet, very similar in appearance to gelatin; this material he called "Tamidine." Such films could be cut automatically with the utmost exactitude, producing filaments of uniform section, which could then be carbonised, before fastening them to the inside of the glass bulb of the incandescence lamp.

Weston was frequently handicapped in his work by the uncertain and time-consuming methods of electrical measurement existing at that time, so he invented for his own use a set of practical measuring instruments. He soon found that there was a great demand for such instruments, so he devoted himself to the art of making accurate, trustworthy, and simple electrical measuring instruments.

What Stas did in chemistry for atomic weights, Weston did for electrical measuring; he created radically new methods of measurement, and introduced an accuracy undreamt of heretofore. His problems were not easy ones. When Weston took up the subject, in 1884, the greatest drawback in the construction and use of accurate measuring instruments was that on account of the so-called temperature coefficient of metals, all measurements had to be corrected by calculation to the temperature at which the observation was made. The favourite metal for resistances at that time was German-silver, but he pointed out that the composition of German-silver varies very considerably. Therefore he proposed a standard copper-nickel-zinc alloy containing about 30% of nickel, and which had a specific resistance of more than twice that of ordinary German-silver and a much lower temperature coefficient. He then took up the systematic study of a large number of alloys, and in the course of the work observed remarkable properties in some manganese alloys: he first produced an alloy which had 65 times the resistance of copper, then an alloy which had no temperature coefficient whatever, and finally, produced several alloys which had a *negative* temperature coefficient. He also showed that the resistance of these alloys depended not only on their composition, but on certain treatments which they undergo, for instance, preliminary heating. After the Weston patents had been published, his alloy was called *manganin* in Germany, and publicity had been given to its properties with scant reference to its real inventor.

No less important was the invention of the Weston standard cell, which since 1908 has become the accepted universal practical standard for electromotive force. Until that time the Clark cell had been accepted as the standard of electromotive force. Weston set himself to make a cell that had no temperature coefficient and had no "lag." He found that the saturated solution of zinc sulphate in which was suspended an excess of crystals of this salt, was an unsuitable electrolyte and one of the principal causes why the

indications of the Clark cell varied considerably with the temperature. He came to the conclusion that cadmium sulphate was more appropriate than the zinc salt, and this was one of the several important improvements he introduced in the construction of a new standard of electromotive force.

Dr. Weston assures me that he has succeeded in making his alloys to show only a change of one-millionth part for a variation of  $1^{\circ}\text{C}$ . The metallic alloys he discovered are now used in nearly all kinds of electrical measuring instruments throughout the world.

Dr. EDWARD WESTON said:—When I entered the service of the American Nickel Plating Co., the art of nickel plating was in its infancy, and very little was known about the conditions necessary to carry it on successfully. In general there was no difficulty with the nickel solutions. When properly used they gave good results. The trouble was mainly due to using methods similar to those employed in depositing silver. A nickel deposit cannot be burnished like silver, because it is too hard; consequently it must be polished. The processes then employed in preparing the articles for nickel plating were mechanical. The articles, after they came from the buffs, were dipped in a hot or boiling solution of caustic potash, until the fat was saponified, and a dark coating of oxide was formed on the surface. They were then scoured with a common plater's brush, dipped in rather fine pumice stone, washed in water, and placed either directly in the bath or immersed in a solution intended to remove the last faint trace of oxide which might have been formed during the scouring. In the processes then employed the standard voltage recommended was two volts, that is, two Smee cells. That practice was obviously wrong, because what was necessary was to cover the inferior metal as quickly as possible after it was placed in the solution; if this was not done, secondary reactions were apt to take place between the inferior metal and the nickel in solution, and then the adhesive characteristics of the coating were lost. Hence in reality one of the most important things was to increase the voltage and quickly coat the whole article with a film of nickel, transfer it to a bath in which the voltage was lower, and let the deposition go on until it reached the required thickness. If the article was very large or irregular in shape, or was a long distance from the operation, parts of the surface would get covered with secondary compounds, and any attempt at polishing would cause flaking. Now, when that relatively rough surface was plated, it was necessary to put on a sufficient coat to cover up the scratches. We lost a very large percentage of the nickel in this way, and also a very great deal of time in carefully polishing the nickel coat. The remedy seemed to be obviously chemical cleaning, and putting on the soft metal before placing it in the bath as good a finish as was wanted on the nickel after polishing. The chemical method of cleaning was adopted entirely and is still in use, except that the cleansing of iron or steel articles or other metals not readily acted upon by caustic potash or soda, is done by the aid of electrolysis.

It then occurred to me that it should be possible to get softer nickel, but at first the only way I could do it was by reducing the rate of deposition, keeping down the tendency to the evolution of hydrogen at the cathode. Some years later I found a solution which yielded a nickel deposit with characteristics closely approaching those of good copper. The metal could be rolled and drawn, and I called it "malleable nickel." It was made by using a single salt of nickel. I soon found, however,

that no single salt of nickel could be used for depositing nickel commercially, and no double sulphate of nickel and potassium or any other alkali could be used for depositing nickel. If a solution of a single salt of nickel (chloride, sulphate, bromide, or iodide) is electrolysed, a good deposit of metallic nickel is first obtained, but after a while the deposit becomes darker and darker in colour, until at last there is a tint of green on the surface of the cathode. When that begins, more and more hydrogen is evolved at the cathode until finally the cathode is covered with a green salt. Now the addition of a little sulphuric acid to the solution causes it to begin depositing nickel again. Although all the single nickel salts are acid to litmus paper, if they are electrolysed until the green deposit forms on the cathode they become basic. That led to the invention of a nickel anode and a new solution.

The anode was made from grain nickel mixed with the minimum amount of carbon, with a binder of tar or pitch, the whole being submitted to hydraulic pressure. If the nickel-carbon electrode were broken up there was apparently no change in the size of the grains, although an enormous amount of nickel had been taken out of the electrode. The only observable difference was that by the use of a sharp-pointed instrument it could be cut out in a powdered condition. If a large cast anode is used for some time it will appear to be just the same size as it was originally, but it will bend like a piece of flexible sandstone. Examined under a glass, it will be seen that the colloidal portion has dissolved out and left the crystals.

The solution used was nickel sulphate or chloride, to which boric acid had been added. If an acid had been added which had a tendency to attack the metal to be coated, secondary reactions would have been set up immediately on putting the electropositive metal into the bath.

During my connection with the plating business I discovered that the presence of colloids was often very harmful in nickel solutions, especially double sulphate or chloride solutions. The presence of 0.1% of gelatin in a plating solution is sufficient to produce a black powdery deposit and also a large amount of hydrogen.

*Dynamos.* Originally the platers had a very small equipment of batteries, and these were very cheap; a fair-sized plating establishment could be run with about \$15 or \$20, so that the introduction of dynamos was a very difficult problem as regards first cost. The first dynamo I built was used in my own place in Elm Street, New York. It had two armatures—one for exciting the field magnet, and the other for drawing the arm. The machine had a regulated rheostat consisting of German silver wires wound around the legs of the table. On the magnet-charging armature I had thin wire until I got the current down, and kept all the E.M.F. for running an arc light, so that I had a very powerful machine for my purposes. As soon as the success of that machine had been demonstrated another one was started, and that dynamo ran continuously until a few years ago, when it was destroyed in a fire. Later I built another type of single armature which was more efficient, but still the efficiency from the power standpoint was rather poor. We built about twenty of these. I realised, however, that a cheaper machine than this was necessary for the plating industries. To reduce the amount of work to the minimum and also the amount of material, the machine was almost entirely made in a lathe—cylindrical work. There were only



two parts in the machine which called for a milling machine or plane. I then designed two small machines. One was about four inches in diameter and about six inches long to be sold for \$65 for the use of small platers. Another size was made about 8 in. in diameter and about 6 in. long, the armature being somewhat larger; that was for a good sized plant, and to sell for \$165. Later we built very much larger machines, up to 20 in. (inside diameter of the cylinder carrying the radio magnets between the poles of which the armatures revolved). This machine had a very high output per pound of material and for unit cost.

Many difficulties were encountered in the introduction of dynamos. At that time the platers got ready during the day and ran the baths at night for 12 to 14 hours; so that the solutions and methods had to be changed to produce the same coating in one-quarter the time. The operators did not approve of the innovation, and the question of price was also a great difficulty.

In the *arc light industry* we were confronted with the opposition to the colour of the light. I started with the long arc lamp, but it failed everywhere. I modified the light for the double purpose of modifying the colour and increasing the power efficiency. The amount of light per horse-power was very largely increased by the addition of the substances that caused the flaming arc, and they also tended to keep the light steady.

Arc light carbons were manufactured on a fairly large scale toward the end of my connection with the business, but when we started to work with the arc lamp here we paid \$1.20 a dozen for carbons from France. Of course that price was fatal to the introduction of the electric light. It was a chemical proposition throughout and it required a good deal of hard work. We sold them at from \$12 to \$14 per thousand when we disposed of the plant, and I think that they afterwards went down to from \$6 to \$8 per thousand.

In the arc lamp we were also confronted with a serious mechanical problem, that of getting the regulators to keep all the arcs always of the same length when they were in series, because there must be the same amount of energy on each lamp. Therefore, the resistances of the individual lamps must be almost exactly the same for equal lighting power. That difficulty was overcome in quite a variety of ways by both Brush and myself.

In the *incandescence lamp* the chemical difficulties were vastly greater than the mechanical. One of the first problems to be solved was the irregularity of the filaments made from bamboo or paper. If a defective loop made from any of these substances is put into a hydrocarbon vapour and a current passed through it, the hydrocarbon vapour will be dissociated, and a deposit of carbon will form on the hot spots, so that finally the loop will be repaired and will glow all over uniformly. The next step is to continue the deposition of carbon all over the loop so as to bring the resistance to exactly what is required before it goes into the lamp.

Substantially, every carbon-filament lamp is made by the above process of carbon treatment. The courts have ruled that I did not invent this process. Hiram S. Maxim got the credit for it, but Sawyer got the first patent on it. I had made it very early in the history of the work, long before Mr. Maxim or Mr. Sawyer had any knowledge of it whatever.

However, when filaments were treated by the hydrocarbon method they always failed at one spot—the initial weak spot. We put a lamp between a powerful permanent magnet and passed an alternating current through it, and the loop vibrated at a rate corresponding with the rate of alternation of the dynamo. That was a severe test, but it showed us whether we had completely eliminated the defective spots, because when the loop began to vibrate if there were any weak spots they would show.

I then took up the problem of producing the structureless homogeneous carbon thread, of uniform cross section, and of uniform electric resistance from end to end for any given section.

After numerous attempts, it was decided to make the filaments from collodion, but the alcohol-ether solvent caused trouble, owing to shrinkage and pitting; this was avoided by very slow evaporation. Finally ammonium sulphhydrate was selected as the most suitable agent for re-forming the cellulose. The process was later modified by squirting a solution of cellulose containing zinc chloride through very fine tubes into alcohol. In that way the homogeneous carbon filaments were obtained.

*Alloys.*—The alloys at our disposal for electrical measurement work were German silver and platinum silver, which was too expensive for use. German silver generally had a resistance about thirteen times that of copper and a temperature coefficient of 0.004133; it contains from 1 to 18% Ni. I found out quite early that it varied very much in resistance, and in temperature coefficient, and that by increasing the percentage of nickel the specific resistance was increased in nearly the same proportion, and the temperature coefficient was reduced by nearly the same proportion. We made standard German silver containing 30% nickel; it had twenty-eight times the specific resistance of copper (about thirteen as given by Madison) and the temperature coefficient was almost half that of copper. These temperature coefficients were of very great importance because it was necessary where electrical instruments were used to give true results, whereas the results obtained from other alloys varied. The very best German silver that we could make was not good enough for instrument work, nor was it good enough for a standard. I therefore examined a large number of alloys, and found that none gave such a high specific resistance as manganin. Nickel stands next to it; it gives very high specific resistance not only with copper but with other metals. On the other hand, the nickel alloys have not so good a temperature coefficient as the manganin alloys, and they have a relatively high thermo-electrical effect against copper and other metals.

*The standard cell.* My first efforts were devoted to the improvement of the Clark cell. According to Clark there was no difficulty in making or selling standard cells of this type. I found a great deal of difficulty, and after quite a long investigation I abandoned the form of cell that Clark used. He recommended making the paste of zinc sulphate, mercurous sulphate, and metallic mercury. I started my cadmium cell and after a long, tedious investigation I finally succeeded, but the lag was very pronounced. I reduced the temperature coefficient of that cell very much and got rid of the lag by using a saturated solution of zinc sulphate which gave a very steady and reliable standard, but still it had a temperature coefficient; to avoid that I used a cadmium mercury amalgam on one side, and pure mercury with mercurous sulphate on the other. This cell with a solution of cadmium sulphate saturated at 4° C. shows practically no temperature coefficient.

### Obituary.

#### JAMES HARGREAVES.

English chemical technology has lost one of its most notable personalities by the death, on April 4th, of Mr. James Hargreaves of Widnes, an original member of this Society.

Born in 1834, he commenced work on the recovery of sulphur from alkali waste in 1859, and in the course of this work became acquainted with William Gossage, who had been experimenting on similar lines. At that time little encouragement was offered by alkali makers to continue the work, though many years afterwards this pioneer work was applied successfully in a somewhat modified form. Entering the employ of Mr. Gossage, Hargreaves turned his attention to the oil and soap industries, and succeeded in devising a process for recovering chromates used in bleaching oils and fats for soap making, by which the cost of the process was very greatly reduced. He also practically revolutionised soap making by discovering a method for bleaching the brown soap in general use at that time, and was the first to prepare blue mottled soap. After leaving Gossage in 1863, he became interested in metallurgical work, and his suggestion to utilise sodium nitrate in place of air in making steel by the Bessemer process, was tried at Nottingham, but though the results were good the method proved too costly. He devised a method for recovering the phosphorus as sodium phosphate from blast-furnace slags, obtaining ferric chloride as a by-product, which was converted direct into the oxide and chlorine. In 1873, he erected works at Widnes to carry out his process for the production of hydrochloric acid by the action of pyrites burner gases on common salt, and this process was run successfully for many years, until the works were taken over by the United Alkali Co.

In conjunction with the late Mr. Thomas Bird, he invented an electrolytic process for decomposing salt, known as the Hargreaves-Bird process. After prolonged experiments, a large cell was constructed and worked continuously for two years, during which time the production was 95½% of that theoretically possible. Later a plant was erected at Middlewich, where the process was carried out on a large scale with great success: these works have recently been

acquired by the Electro-Bleach and By-Products, Ltd. The process has also been extensively adopted in Europe and America with very satisfactory results.

#### J. M. C. PATON.

Mr. J. M. C. Paton, Managing Director of Messrs. Manlove, Alliott and Co., Ltd., Nottingham, died on April 10th, after a short illness. Mr. Paton always took a keen and active interest in the affairs of this Society, and especially of the Nottingham Section, of which he was Chairman from 1893 to 1895. He also served on the Council of the Society as an Ordinary Member from 1899 to 1901 and as Vice-President from 1901 to 1903.

#### OTTO N. WITT.

Otto Nikolaus Witt was born in Petrograd on March 31st, 1853. He studied chemistry at the Zurich Polytechnikum and graduated at Zurich University. After spending some years in honours in Germany and in calico print-works in Switzerland, he came to England, where he was engaged at the works of Williams, Thomas, and Dower, Brentford. Later he returned to Germany to work at the dyestuff factory of L. Cassella und Co., and in 1894 he was appointed Professor of Chemical Technology at Charlottenburg.

From the year 1876 onwards, Witt contributed largely to our knowledge of the dyestuffs. He was one of the first to attempt a correlation of the colour and other properties of dyestuffs with their constitution, and it was he who showed that the tinctorial properties of certain aromatic compounds depend upon the presence both of a chromophore and of a salt-forming group, and that the tinctorial power of a dyestuff increases with the number of chromophoric groups present. Among the azo dyestuffs his work included the preparation of chrysoidine and the tropaeolins. In the azine series, he discovered the eurihodines and eurihodols, and prepared a number of new safranines and higher indulines. In 1881 he discovered the indophenols and also prepared their leuco compounds.

Witt was one of the foremost German technologists, and acted as President of the International Congress of Applied Chemistry held in Berlin in 1903. He was an original member of this Society. He died suddenly on March 23rd.

## Journal and Patent Literature.

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### I.—GENERAL PLANT; MACHINERY.

#### PATENTS.

*Centrifugal separator.* E. Köpke, Honolulu, Hawaii, Assignor to Köpke Clarifier Co., Ltd. U.S. Pat. 1,119,173, Dec. 1, 1914. Date of appl., Dec. 8, 1911.

Is a centrifugal separator for the clarification of liquids by stratification, cross-currents converging

towards the discharge, which would tend to disturb the established strata, are prevented by placing a permeable partition (perforated plate, wire netting, cloth) within the rotor in the path of the overflow therefrom and adjacent to the discharge opening, whereby the discharge is broken up into a multitude of small jets spread over a considerable area, the direction of the flow of liquid through the screen being preferably opposite to the direction of the centrifugal force.—J. F. B.

*Centrifugal separator.* E. Köpke, Honolulu, Hawaii. U.S. Pat. 1,119,176, Dec. 1, 1914. Date of appl., June 21, 1912.

THE rotating bowl, constituting an imperforate stratifying chamber, is provided near the bottom with an annular guide plate, preferably inclined downwards, and forming an antechamber into which the crude liquid is first introduced. The periphery of the guide plate extends near the wall of the bowl, so that the liquid issuing from beneath it enters the stratifying chamber at a level well below the surface of the body of liquid undergoing stratification. The space between the guide plate and the floor of the drum is enclosed by a perforated screen, whereby the liquid passing beneath the guide-plate is broken up into a number of small streams. The clarified liquid may be discharged over the overhanging lip of the bowl or by means of an adjustable scoop.—J. F. B.

*Separating solids from liquids; Centrifugal machine for —.* Jahn und Co. Fr. Pat. 471,531, April 30, 1914. Under Int. Conv., May 3, 1913, and April 8, 1914.

SEE U.S. Pat. 1,124,907 of 1915; this J., 1915, 264. The telescopic outlet tubes are so adjusted that the solids are discharged by the action of the pressure in the drum without the use of conveyors.—W.H.C.

*Filtration: Process and apparatus for —.* Soc. des Etablissements Daubron. Second Addition, dated July 17, 1913, to Fr. Pat. 437,614, Feb. 22, 1911 (this J., 1912, 524).

THE filter cloth is covered with coarse canvas, so that when the filter is cleaned by reversing the current, the rubbing of the canvas against the filter cloth assists in the discharge of the deposit. —W. H. C.

*Filtration; Apparatus for —.* C. Butters and Co., Ltd. Fr. Pat. 472,015, May 9, 1914. Under Int. Conv., Aug. 13, 1913.

THE bag of filter cloth which surrounds the frame of a suction filter is left open at the bottom, the ends hanging down below the lower part of the frame, so that when the filter is under suction, they are drawn together, and close the bag. When water is admitted to the interior of the frame to discharge the cake, the lower ends of the bag open and allow the pressure within and without the frame to be equalised.—W. H. C.

*Filtration; Process and apparatus for —.* C. Butters. Fr. Pat. 472,017, May 9, 1914. Under Int. Conv., June 18, 1913.

A RAPID current of the liquid or mud to be filtered is caused to flow over the surface of horizontal suction filters mounted on a frame, so that the formation of the cake is assisted by the action of gravity. To aerate the mud, it is supplied faster than the filters can receive it, and the portion which overflows is re-circulated. When the cake is sufficiently thick it is washed, and the filters are tilted to discharge the cakes.—W. H. C.

*Mixing and disintegrating apparatus.* J. Woltersdorf. Fr. Pat. 471,661, March 31, 1914.

AN axial shaft passing through a horizontal cylindrical casing carries at the ends two oppositely threaded screw conveyors and, in the middle, a series of beater arms projecting into the spaces between flat or wedge-shaped teeth fixed to the inner wall of the casing. Material fed into the casing is delivered by the conveyor screws to the beaters of the disintegrator, and the mixed product is discharged through a door on the lower side of the casing controlled by a spring.—W. H. C.

*Disintegrators; Process and means for increasing the output of —.* G. Polysius. Fr. Pat. 471,675, April 7, 1914. Under Int. Conv., April 9, 1913.

To increase the output of disintegrators, the particles which are too large to pass through the sieves are collected by hook-shaped projections on the interior surface of the drum, and are carried round and returned to the sphere of action of the beaters when the projections reach the lowest point of their path.—W. H. C.

*Filtering apparatus.* M. Deacon and W. Gore, London. U.S. Pat. 1,130,382, March 2, 1915. Date of appl., Dec. 3, 1912.

SEE Eng. Pat. 29,301 of 1911; this J., 1913, 221.

*Furnace tubes or chambers; Manufacture of —.* R. P. Pictet, Walsall. U.S. Pat. 1,130,533, March 2, 1915. Date of appl., July 30, 1914.

SEE Eng. Pat. 15,379 of 1913; this J., 1914, 849.

*Dust from air or vapour; Apparatus for extracting —.* J. Herbing, Halle, Germany. U.S. Pat. 1,130,596, March 2, 1915. Date of appl., Oct. 3, 1913.

SEE Eng. Pat. 20,700 of 1913; this J., 1914, 468.

*Liquids from solids; Apparatus for, and method of expressing —.* J. J. Berrigan, Orange, N.J., Assignor to H. R. Worthington. U.S. Pats. 1,130,701 and 1,130,879, March 9, 1915. Dates of appl., Aug. 22, 1911, and July 8, 1913.

SEE Eng. Pat. 18,584 of 1912; this J., 1913, 933.

*Drying objects formed of plastic masses; Method of —.* O. Eberhard, Heidenau, Germany. U.S. Pat. 1,131,047, March 9, 1915. Date of appl., Aug. 8, 1912.

SEE Fr. Pat. 455,959 of 1913; this J., 1913, 933.

*Centrifugal separator.* U.S. Pat. 1,119,175. See XVII.

## IIA.—FUEL; GAS; MINERAL OILS AND WAXES.

*Coal and petroleum; Some relations in origin between —.* D. White. U.S. Geol. Survey. J. Washington Acad. Sci., 1915, 5, 189–212.

FROM a consideration of the specific gravities of the oils, and the various degrees of regional alteration exhibited by the mother rocks and associated carbonaceous deposits, of different geological formations and regions in the Eastern United States, it is concluded that petroleum results from the geodynamic alteration of certain types of organic debris deposited in sedimentary strata. The types of oils produced are probably governed by the composition of the original organic deposits, and the rank of the oils within each type by the stage to which the natural distillation has progressed. Oils of the lowest rank of each type usually occur in those regions and formations in which the carbonaceous deposits are least altered, and oils of the highest rank in regions where the carbonaceous deposits are of correspondingly high rank, the effect of progressive regional dynamic alteration being marked by a concentration of hydrogen in the oils and a concentration of carbon in the residual débris (coal, carbonaceous shale, etc.). The sporadic occurrence of abnormally light oils in pools of lower rank is probably due to filtration, or to migration from underlying

formations of more advanced alteration. In general, at a given point, the oils found in successive underlying formations, or stratigraphically lower sands in the same formation, are progressively higher in rank. Engler's principle—that the increase in sp. gr. of the oil is inverse to the stratigraphical depth of the well—thus corresponds to Hilt's law with regard to the increasing carbonisation of coals with depth. In regions where the progressive removal of volatile substances from the organic deposits in any formation has passed a certain point, marked in most provinces by 65 to 70% of fixed carbon (pure coal basis) in the associated or overlying coals, commercial oil pools are not present in that formation or in any other formations normally underlying it, although commercial gas pools may occur in a border zone of higher carbonisation. The approximate carbonisation limits of the rocks containing or overlying oil pools may vary somewhat in different provinces according to the characters of the original organic debris, the circumstances attending its deposition, and the geological structure. Wherever the regional alteration of the carbonaceous residues passes the point marked by 65–70% of fixed carbon, the light distillates appear, in general, to be gases at rock temperatures. Occluded oils may, in some cases, have escaped volatilisation.

—W. E. F. P.

*Calorimetry; Combustion —, and the heats of combustion of sucrose, benzoic acid, and naphthalene.* H. C. Dickinson. Scientific Papers of Bureau of Standards, U.S.A., No. 230, July 16, 1914. Bull. Bureau Standards, 1914, 11, 189–257.

THE sources of error in bomb calorimetry can be avoided or reduced to a negligible quantity by care in the design, construction, and use of the calorimeter. The cooling corrections for a properly designed calorimeter may be made with an accuracy of about 1 part in 10,000 of the total amount of heat measured. Determinations of the heat of combustion of naphthalene gave  $9622 \pm 2$  calories per gram, weighed in air, with a maximum deviation of about 5 in 10,000 for groups of observations upon the same sample, and about the same maximum deviation of different groups of observations from the mean of all, regardless of the sample. Benzoic acid gave  $6329 \pm 1$  calories ( $20^\circ$ ) per gram, weighed in air, with a maximum deviation of about 1 in 1000 for the earlier experiments and 5 in 10,000 for the later ones. Sucrose gave  $3949 \pm 2$  calories ( $20^\circ$ ) per gram, weighed in air, with a mean deviation of about 3 in 10,000. Benzoic acid is regarded as the most desirable substance for a combustion standard as indicated by the agreement between the results of different observers. Naphthalene is very reliable and convenient although it requires care in handling. Sucrose is not so satisfactory as benzoic acid because of its lower heat of combustion, its frequent failure to ignite, and the lower precision of the results obtained.—E. R. A.

*Bunsen flame; Combustion in the inner cone of the —.* L. Ubbelohde and O. Dommer. J. Gasbeleucht., 1914, 57, 757–765, 781–787, 805–810. Z. angew. Chem., 1914, 27, Ref., 729–730.

Dixon's observation that the presence of water vapour is necessary for the explosion of mixtures of carbon monoxide and oxygen is confirmed. The maximum accelerating effect is obtained with 7–10% of steam in the case of mixtures of carbon monoxide and air. In experiments with a carbon monoxide-air flame, equilibrium was not established at a point immediately over the inner cone. The velocity of the trimolecular reaction,  $2CO + O_2 = 2CO_2$ , was greater at the surface of the

inner cone than in the region outside the cone. By the use of platinum gauze or an incandescence mantle, combustion can be accelerated so that equilibrium is attained. The temperature of a carbon monoxide-air flame measured thermoelectrically is lower than the theoretical temperature calculated from calorimetric data, so that in practice a mixture of carbon monoxide and hydrogen, though less efficient theoretically, will give a higher flame temperature than carbon monoxide alone. Experiments were also made with flames of air with hydrogen, methane, acetylene, and lighting gas, respectively, and in no case was the dissociation equilibrium attained.—A. S.

*Gases; Separation of — by fractional distillation in a vacuum at low temperatures.* G. A. Burrell and I. W. Robertson. J. Ind. Eng. Chem., 1915, 7, 209–210.

A RESUME of the authors' work on the subject (see also this J., 1914, 808; 1915, 17, 267). In the case of mixtures of paraffin hydrocarbons, the methane is distilled at the temperature of liquid air, ethane at not above  $-140^\circ$  C., propane at not above  $-120^\circ$  C., and butanes at not above  $-95^\circ$  C. From mixtures of olefines ethylene is distilled at not above  $-140^\circ$  C. and propylene at not above  $-120^\circ$  C. When paraffins and olefines are both present, ethane and ethylene, and propane and propylene are removed together, and the proportion of each in the mixture is determined by combustion. Benzene vapour in air or gaseous mixtures such as coal gas may be distilled at the temperature of liquid carbon dioxide ( $-78^\circ$  C.), after removing the other constituents at lower temperatures, and its amount estimated from its pressure. Gasoline vapour in air is determined at the temperature of liquid air. Water vapour in air can be determined at  $-78^\circ$  C. The distillates must be refracted several times to obtain pure fractions.—A. S.

*Gases; A rapid method of fractionating — at low temperatures.* G. A. Burrell and I. W. Robertson. J. Ind. Eng. Chem., 1915, 7, 210–211.

THE gaseous mixture is fractionated at progressively increasing temperatures, then the first distillate is refracted at the lowest temperature used, the second fraction added to the residue and fractionated at a somewhat higher temperature, and so on, the essential difference from the original method (see preceding abstract) being that the successive fractions are added to the residue in the liquefying bulb instead of each fraction separately being redistilled several times.—A. S.

*Gasoline and aromatic hydrocarbons; New process of obtaining — from crude petroleum.* Oil, Paint, and Drug Rep., March 8, 1915.

THE Secretary of the Interior Dept., U.S.A., has given some general details of Rittman's process of obtaining gasoline, benzol, and toluol from petroleum, which is about to be patented in the name of the United States. The process differs from that of Burton (this J., 1914, 911), in that the vaporised oil is passed downwards through an iron tube in which it is heated under pressure, and then through a condenser from which the liquefied products are withdrawn. For the production of gasoline the oil vapours are heated to  $450^\circ$  C. and upwards under a pressure of 90 lb. per sq. in., whilst for the production of benzol and toluol a temperature of  $500^\circ$  C. and pressure of 100 lb. per sq. in. are required. The greater the proportion of gases in the tube the higher is the yield of liquid products. In laboratory experiments about 80% of a heavy oil residue was utilised, and by repeated passage through the tube yielded about 8% of gasoline. A single passage of the oil through the

tube yielded about 6% of aromatic hydrocarbons, and it is anticipated that in the commercial process the yield will be 6 to 10 times greater than the quantity obtained from coal tar. It is stated that the objectionable odour of the gasoline made by Burton's process has been eliminated, and that the product is now a practicable substitute for petrol.—C. A. M.

*Gasoline and kerosene from heavier hydrocarbons; Preparation of*——. B. T. Brooks, R. F. Bacon, F. W. Padgett, and I. W. Humphrey. *J. Ind. Eng. Chem.*, 1915, 7, 180—185.

VARIOUS patented processes for the cracking of petroleum are reviewed briefly, and, in connection with the proposed use of nickel as catalyst, attention is called to the work of Ostromisslenski and Bujanadse (this J., 1910, 682) who found that Russian crude petroleum when heated at 600°—700° C. in presence of nickel was converted entirely into coke (40%) and gas, the latter consisting of hydrogen (72—75%) and saturated hydrocarbons. In the authors' experiments kerosene and solar oil vapours were passed, at atmospheric pressure, through an iron tube filled with a contact substance and heated to 500°—550° C.: the olefine content of the gasoline fractions obtained with burnt clay, carbon, iron, or copper as contact substance was 25—30%, but with nickel it was 48%. Burton's claim (U.S. Pat. 1,049,667; this J., 1913, 414) that in cracking petroleum under pressure olefines are not produced if the pressure-controlling valve is placed beyond the condenser instead of between the condenser and the still, could not be confirmed. The olefine content is diminished by increasing the pressure, and in Bacon and Clark's process (U.S. Pat. 1,101,482; this J., 1914, 824) the use of 100—300 lb. pressure per sq. in. is claimed. In experiments with Oklahoma crude petroleum from which the gasoline and kerosene had been removed, the yield of gasoline distilling below 150° C. increased with rise of pressure to a maximum of about 33% at 280 lb. per sq. in. pressure, and then slowly diminished, whilst the refining loss on treatment with concentrated sulphuric acid diminished as the pressure was increased up to about 200 lb. per sq. in. and then remained practically constant. According to Bacon, Brooks, and Clark (U.S. Pat. 1,131,309), within certain limits the cracking effect is approximately proportional to the heating surface in contact with the oil, and the amount of coke deposited on vertical heating surfaces is only from one-third to one-fifth of that deposited on an ordinary still bottom. The fraction of b. pt. 200°—250° C. obtained by cracking at 100 lb. pressure Oklahoma petroleum from which the gasoline and kerosene had been removed, showed an optical activity of +0.36° on the saccharimeter scale in a 400-mm. tube; the corresponding fraction from the original oil had an activity of +0.2° in a 200-mm. tube. The gasoline obtained by cracking at 100 lb. pressure contained aromatic hydrocarbons: benzene, toluene, and xylene were identified by the formation of 1,3-dinitrobenzene, 2,4-dinitrotoluene, and 2,4,6-trinitro-*m*-xylene respectively. It is suggested that the aromatic hydrocarbons are formed from petroleum hydrocarbons containing the phenyl group, derived probably from protein substances. Only small quantities of naphthenes were present in the gasoline, the predominating constituents being normal paraffin hydrocarbons.—A. S.

*Petroleum; Analytical distillation of*——. W. F. Rittman and E. W. Dean. *J. Ind. Eng. Chem.*, 1915, 7, 185—195.

THE authors give the results of a comparison made in the U.S. Bureau of Mines of different methods

of distilling petroleum for analytical purposes. The methods selected were that of Allen and Jacobs (this J., 1912, 18), in which the entire surface of the distilling flask is heated electrically so that no condensation occurs in the vapour space of the flask; the Engler-Ubbelohde method, in which there is a moderate amount of condensation in the distilling flask, and the Hempel method, using a flask with the fractionating column made in one piece with the bulb (Dean and Bateman, *Bull.* 112, Forest Service, U.S. Dept. Agric.); aluminium beads were found more satisfactory than glass ones for filling the column. The detailed results are given in tables and diagrams. A much higher degree of fractionation was obtained by the Hempel method than by either of the others, and the method of Allen and Jacobs was the least efficient. A single distillation with a Hempel column was more efficient than two successive distillations by the Engler-Ubbelohde method. The degree of separation increased with rise of temperature, and the amount of this increase could be ascertained roughly by determination of the specific gravities of the fractions. Even the Hempel method, however, gave but a low degree of separation, for on redistillation only about 55% of a given fraction came over within the original temperature limits; for the Engler-Ubbelohde and Allen and Jacobs' methods the corresponding figures were 25 and 14% respectively.—A. S.

*Petroleum residuum; Variations of the physical characteristics of a*——with increasing percentages of grahamite. H. Rossbacher. *J. Ind. Eng. Chem.*, 1915, 7, 205—206.

THE effects produced on the physical properties of a Mexican petroleum residuum by addition of up to 30% of grahamite are shown in a table and diagrams. The relation between the melting point and the percentage of grahamite in the mixture was practically linear. The mixtures were tested with a penetrometer at different temperatures: the temperature-penetration curves all showed a tendency to flatten out far below the melting point, indicating that too much reliance should not be placed upon the melting point or upon the penetration at one particular temperature in judging the value of an asphaltic material. The temperature-penetration curve of the mixture containing 15% of grahamite corresponded closely with that of the residue left when the original petroleum residuum was subjected to a 20-hour evaporation test at 485° F. (252° C.).—A. S.

*Trinidad asphalt.* C. Richardson. *J. Phys. Chem.*, 1915, 19, 241—249.

THE oil sands occurring at different depths in the locality of the mud spring in the island of Trinidad contain a highly asphaltic petroleum, which, upon meeting the fine silica and clay mud of the spring, is emulsified by the action of the natural gas under high pressures, forming the so-called "soft pitch." The natural gas contains, in addition to hydrocarbons, as much as 33% CO<sub>2</sub> and 3.5% H<sub>2</sub>S. The "soft pitch" also slowly evolves gas and gradually hardens, the process being possibly catalysed by adsorbed ferrous sulphate. The approximate composition of the crude asphalt, which is remarkably homogeneous, is: water and gas 29.0%, bitumen soluble in cold carbon bisulphide 39.0%, bitumen adsorbed and retained by the disperse mineral matter 0.3%, mineral matter on ignition with tricalcium phosphate (see this J., 1909, 419) 27.2%, water of hydration of clay 4.2%. The water obtained from the melted material contains about 20 grms. of salts per litre, including sodium, ferrous, and ammonium sulphates, sodium chloride, and small amounts of iodides and borates.

The mineral matter obtained on ignition consists of impalpably fine silica, clay, and the non-volatile salt residue. The preparation from the asphalt, by means of carbon bisulphide and other organic solvents, of a bitumen free from mineral matter is rendered difficult by the presence of colloidal material, consisting mainly of bitumen adsorbed by clay and other mineral matter in a state of high dispersion; about one-half of the bitumen is soluble in naphtha of 88° B. (sp. gr. 0.621), and this portion is not adsorbed. The crude asphalt thus consists of "a suspension of relatively large size mineral particles in an extremely viscous medium, together with highly dispersed mineral matter in colloid form, intimately mixed with an emulsion of a thermal water with the bitumen present." A very similar product results when a crude Bermudez asphalt, practically free from mineral matter, is softened below 100° C. and emulsified with a paste of colloidal clay and water. The presence of suspensoid and dispersoid material in asphalt enhances the surface energy and viscosity and lessens the ductility and susceptibility to change of temperature; the effect of an added mineral dust, though of the same nature, is far less than that of the highly dispersed colloids which are present in Trinidad asphalt.—J. R.

*Melting point of paraffin waxes; Apparatus for determining the*—F. H. Small. J. Amer. Leather Chem. Assoc., 1915, 10, 141—146.

A narrow graduated glass tube, closed below by a cork, is fused at its upper end to a wider tube provided with a loosely-fitting plunger and containing the shaved wax, on which rests a weight. The whole is immersed in a bath of water which is heated gradually, the temperature being kept constant for 7 minutes after each degree rise. The amount of melted wax which collects in the narrow graduated tube is noted after each degree rise of temperature, the plunger being slightly raised and lowered to facilitate the flowing of the melted wax. The temperature at which 50% of the wax is melted corresponds to the melting point as usually determined.—T. C.

#### PATENTS.

*Peat pulp or the like; Apparatus for heating*—The International Nitrogen and Power Co., Ltd., E. A. Buckle, and O. D. Lucas, London. Eng. Pat. 5815, March 7, 1914.

In carrying out the process described in Eng. Pat. 10,370 of 1912 (this J., 1913, 590), the peat is heated by forcing it through tubes passing longitudinally through horizontal water cylinders connected to horizontal cylindrical boilers arranged beneath them. The boilers are heated by hot gases which pass through internal tubes and emerge into a chamber enclosing the whole apparatus.—W. F. F.

*Coal-washing apparatus.* E. G. Burks and N. Hayes, Birmingham, Ala. U.S. Pat. 1,132,433, March 16, 1915. Date of appl., July 3, 1914.

The wash water is passed through a settling tank provided with two partitions forming a pair of inlet chambers, between which is a tortuous trough. The wash water passes from a sluice above the tank into each of the inlet chambers and into the trough. Liquid is discharged from the tank at variable levels through a stand-pipe.—W. F. F.

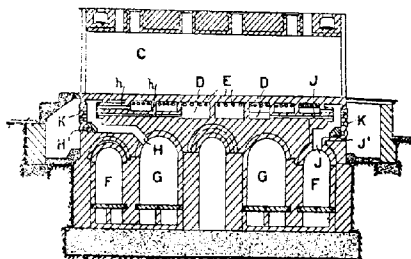
*Coal briquettes; Carbonisation of*—B. Grütz. Fr. Pat. 472,402, May 19, 1914. Under Int. Conv., Jan. 26, 1914.

COAL briquettes containing a carbonaceous binding medium are heated to incipient coking in a revolving drum or series of superposed drums

placed in a current of hot gas, and then pass through a shoot into a larger drum revolving more slowly in a casing, of which one side only is subjected to the hot gas. The coking is completed in this large drum.—W. F. F.

*Coke-ovens; Gas-fired*—Simon-Carves Bye-Product Coke Oven Construction and Working Co., Ltd., and J. H. Brown, Manchester. Eng. Pat. 29,367, Dec. 20, 1913.

In a coke-oven adapted to be fired either with rich or poor gas, combustion flues extending longitudinally between the coking chambers, C, are fed



with rich gas from channels along their base, and with air from one set of regenerators, F, G, through the ducts, H, h, D, the flow being regulated by the fireclay plug, H'. Poor gas may be supplied through the regenerator, F, to ducts, D, under one coking chamber, the corresponding ducts under the next chamber being still supplied with air from the regenerator, G; both sets of ducts open into each combustion flue. The combustion products pass through both regenerators, F, G, of the other set, so that the usual reversal may take place.—W. F. F.

*Coke; Removable grate for shaft furnaces for the continuous production of*—W. Schwarz. Ger. Pat. 280,985, Oct. 1, 1913.

The grate bars, with pointed ends, are arranged symmetrically around the periphery of the furnace, and are fixed, e.g., in sets of three, to spindles provided with screw threads. Each spindle works in a thread on the inside of a cog-wheel, and the whole of the cog-wheels may be operated simultaneously by a large toothed wheel, whereby the bars are moved into or withdrawn from the furnace in a radial direction.—A. S.

*Retorts for carbonising coal or the like; Mechanism for charging horizontal or inclined*—A. McD. Duckham, Ashted, Surrey. Eng. Pat. 13,936, June 9, 1914.

In apparatus having a plunger reciprocating over a coal shoot in front of the retort, a sleeve moves ahead of the plunger to enclose a core of fuel and prevent jamming.—W. F. F.

*Coal gas retort chambers and the like; Heating*—A. G. Glasgow, Richmond, Va., U.S.A. From J. M. Rusby, Philadelphia, Pa., U.S.A. Eng. Pat. 22,425, Nov. 12, 1914.

The chamber is heated by producer gas, generated by passing air through a burning bed of fuel, the production of clinker being prevented by passing a regulated supply of steam through the fire. The temperature of the chamber is controlled by adding an incombustible diluent, e.g., the products of combustion, to the burning producer gas.—W. F. F.

*Gas furnaces; Process and apparatus for heating*  
—either by producer gas or lighting gas.

R. Geipert. Fr. Pat. 471,644, Mar. 20, 1914.  
Under Int. Conv., April 14 and Nov. 1, 1913.

DURING the use of lighting gas in gas furnaces which may be heated alternatively by producer gas or lighting gas, the producer is kept hot by the production of a small quantity of gas which is burnt with the lighting gas. The producer may be connected to the furnace by a permanently open conduit for this purpose, and by others which are temporarily closed. To avoid the passage of large quantities of producer gas to the furnace during cleaning, the lighting and producer gas conduits may be partially closed. The lighting gas may be passed through the incandescent fuel in the producer to destroy the illuminants.—W. F. F.

*Gas producers; Ash-discharging device for —.*  
Q. Moore, Glasgow, and The Dowson and Mason Gas Plant Co., Ltd., Manchester. Eng. Pat. 2649, Feb. 2, 1914.

A DEVICE whereby any accumulation of ash at either the ends or the middle of producers—of the type which, in sectional plan, are considerably greater in length than in width (Eng. Pat. 28,054 of 1908)—may be discharged from the ash table into a hopper without interfering with the other parts. Above the ash table is an oscillating shaft carrying a plate made in sections and depending towards the table. One or more of the sections are hinged to the shaft and the others to sleeves on the shaft.—E. R. A.

*Producer-gas; Manufacture of —.* L. E. Hirt. Pittsburgh, Pa. U.S. Pat. 1,130,512, March 2, 1915. Date of appl., Feb. 25, 1913.

OIL is sprayed into a combustion chamber by means of steam, and the combustion products pass through a contracted passage into an expansion chamber, and then if required through another contracted passage to a second expansion chamber, the total expansion being at least five-fold. The gas next passes through a relatively narrow passage in contact with incandescent carbon on the walls, and then steam is injected into it.—W. F. F.

*Producer for hot gas.* E. Fleischer. Fr. Pat. 471,341, Apr. 25, 1914. Under Int. Conv., Sept. 19, 1913.

THE process for the production of hot gas from non-bituminous fuel described in Fr. Pat. 422,699 (this J., 1911, 529) is modified for use with bituminous fuel. The producer chamber is formed of three superposed compartments of the shape of inverted cones. The hot producer gas is withdrawn from the lowest compartment, but a small part is allowed to pass upwards through the intermediate zone containing fuel almost completely coked. Secondary air is supplied to the upper part of this zone, and the burning gas passes upwards through the upper compartment and carbonises the raw fuel, the gaseous products being drawn off at the top.—W. F. F.

*Gas-producer; Electrically heated.—.* G. Coutagne. Fr. Pat. 471,582, July 15, 1913.

AIR, or a mixture of air and steam, is passed through a mass of coal in a vertical retort, the coal being heated by an electric current passing between two electrodes, one of which is tubular and forms part of the wall of the retort, whilst the other is a central rod adjustable vertically to vary the current.—W. F. F.

*Gas producers; Process for increasing the total output and yield of ammonia of —.* H. Koppers. Ger. Pat. 279,550, Sept. 20, 1913.

A COMBUSTIBLE gas (hydrogen, producer gas) is used, together with a mixture of steam and air, as

diluent for the purpose of increasing the yield of ammonia, and the process is conducted at such a high temperature that the gas introduced burns continuously, and thus maintains the temperature of the reaction zone. The process may be applied to retort furnace installations heated by producer gas, in which case the gas, consisting chiefly of hydrogen, produced during the last stage of distillation, is led off separately and introduced into the gas producer.—A. S.

*Gas; Production of — from finely divided fuels.*  
F. Clauss. Ger. Pat. 279,691, Nov. 2, 1913.

A PART or the whole of the gas produced is passed again into the retorts, and the heat required for gas production is supplied by heating the gas outside the retorts, by heating the retorts externally, by burning part of the gas within the retorts, or by increasing the pressure in the retorts. The fuel is introduced into the retorts along with the portion of the gas which is returned.—A. S.

*Gas; Process and apparatus for purifying [filtering]*  
— H. F. Smith. Fr. Pat. 472,306, May 16, 1914.

To remove tar and the like, the gas is passed through a diaphragm of glass wool at such a speed that the fibres are electrified. The very small particles are attracted to the fibres, or are carried through and coalesce into larger drops, being then removed by another filter. Large particles which are retained are removed by the gas stream on reversing the diaphragm.—W. F. F.

*Motor fuel; Production of —.* W. A. Hall. New York. Eng. Pat. 2948, Feb. 4, 1914.

HEAVY hydrocarbon oil is cracked at about 600° C. till about 25% is converted into gas, composed mainly of hydrocarbons of the ethylene series. The gases are mixed with alcohol vapour and the mixture is liquefied under pressure.—W. F. F.

*Petroleum oils; Apparatus for distilling —.*  
J. B. Moore, Whiting, Ind., Assignor to Standard Oil Co., Chicago, Ill. U.S. Pat. 1,130,318, March 2, 1915. Date of appl., Oct. 19, 1914.

A LONG, inclined, air-cooled pipe extends upwards from the still to the lower end of a condenser, the upper end of which is connected to a second condenser by a pipe extending downwards. A valved by-pass connects the two vapour pipes.—W. F. F.

*Petroleum; Fractional condenser for separating hydrocarbons in distilling —.* J. W. Van Dyke and W. M. Irish, Assignors to The Atlantic Refining Co., Philadelphia, Pa. U.S. Pat. 1,130,862, March 9, 1915. Date of appl., April 18, 1911.

THE hydrocarbon vapours pass through vertical pipes which extend from the top of a chamber to an annular header, and are cooled by air which passes in regulated amount through a surrounding casing. Means may be provided for constricting the pipes and for relieving pressure.—W. F. F.

*Liquid fuel; Process of making —.* C. H. Warth, East St. Louis, Ill. U.S. Pat. 1,131,880, March 10, 1915. Date of appl., Dec. 29, 1913.

A MIXTURE of kerosene and benzol is vaporised in a retort by superheated steam, the heavier liquids are removed by two successive fractional condensations, and the remaining gas is condensed.—W. F. F.

*Mineral oils; Process and apparatus for the treatment of —.* C. Guyard. Fr. Pat. 472,195, May 14, 1914.

IN the decolorisation of mineral oils, especially for the production of vaseline, by filtration through

finely divided argillaceous earth or animal charcoal in a steam-jacketed vessel, filtration is accelerated by means of air or other gas under pressure. The spent filtering material is regenerated in the filtering vessel by treating first with petroleum spirit to dissolve adherent oil and then with benzene to dissolve the colouring matter. The filtering vessel is mounted on trunnions.—W. F. F.

*Gas; Art of removing tarry substances or tar from* — F. W. Steere, Detroit, Mich., Assignor to Somet-Solvay Co., Solvay, N.Y. U.S. Pats. (A) 1,130,212, (B) 1,130,213, and (C) 1,130,214, Mar. 2, 1915. Dates of appl., (A) and (B) Jan. 7, (C) April 24, 1914.

(A) THE gas is passed through an electrical field of alternating polarity, between receiving and discharging electrodes, and is subjected to the action of brush electric discharges from the discharging electrode, which has a pointed surface. The tarry particles coalesce and are deposited on the receiving electrode. (B) The particles of tar are agglomerated as described under (A), and are separated subsequently, the gas being passed at such a high velocity that the agglomerated particles are removed from the electric field with the gas. (C) The gas is heated sufficiently to liquefy the tar and raise the gas above its water-vapour saturation temperature, and is then passed through an electric field of alternating polarity between opposed electrodes.—E. R. A.

*Heavy hydrocarbons; Conversion of — into lighter hydrocarbons.* H. E. Fenchelle and F. M. Perkin, London, Eng. Pat. 6547, Mar. 14, 1914.

HEAVY liquid or liquefied hydrocarbons are cracked by forcing them under high pressure through one or more long, narrow, heated conduits, the resulting liquid being cooled under pressure and then allowed to escape at a relatively lower pressure (e.g. atmospheric) into a chamber surmounted by a rectifying column. By cooling under pressure the lighter hydrocarbons are separated by spontaneous evaporation from the unconverted portion of the liquid; the latter is subjected to further treatment in a still, for which purpose, and for raising steam, the heat abstracted during the cooling process is utilised.—W. E. F. P.

*Petroleum distillation; Art of* — E. M. Clark, Alton, Ill., Assignor to Standard Oil Co., Whiting, Ind. U.S. Pat. 1,132,163, Mar. 16, 1915. Date of appl., Oct. 24, 1914.

PRODUCTS of low b. pt. in the same series are obtained from liquid petroleum distillates of higher b. pt. than 500° F. (260° C.), by effecting cracking and distillation in stages, the liquid in one still being maintained under a pressure of uncondensable gases produced by more advanced cracking and distillation in another still.—W. E. F. P.

*Combustion in chambers containing retorts; Apparatus for controlling* — A. G. Glasgow, Richmond, Va. From J. M. Rusby, Philadelphia, U.S.A. Eng. Pat. 12,257, May 18, 1914. SEE U.S. Pat. 1,106,319 of 1914; this J., 1914, 910.

*Gas; Process of making* — H. Burgi and C. H. Tenney, Springfield, Mass., U.S.A. Eng. Pat. 10,972, May 4, 1914. SEE U.S. Pat. 1,095,806 of 1914; this J., 1914, 585.

*Bituminous fuel; Manufacture of various products (gas, oil, etc.) from* — R. MacLaurin, Stirling, Scotland, U.S. Pat. 1,130,001, March 2, 1915. Date of appl., Oct. 14, 1914.

SEE Eng. Pat. 24,426 of 1913; this J., 1914, 1148.

[Fullers'] earth-treating process. U.S. Pat. 1,132,054. See XII.

## IIb.—DESTRUCTIVE DISTILLATION; HEATING; LIGHTING.

*Radiating bodies (gas fires); A bolometric method of determining the efficiencies of* — W. A. Bone, H. L. Callendar, and H. J. Yates, Proc. Roy. Soc., 1915, A, 91, 245—251.

THE bolometer used consisted of two exactly similar coils of platinum wire wound on thin mica, each 4 cm. square and of 20 ohms resistance, mounted back to back on either side of a circular gun-metal box through which water was circulated. The coils were coated to an even surface with hard, black enamel and could be cleaned without risk of injury; each was provided with a loose cover. When both coils were screened, their resistances remained equal however the temperature of the box changed; but when one was exposed to radiation its resistance was correspondingly increased. The instrument was calibrated by comparison with a radio-balance, the intensity of the radiation required to produce an increase of resistance of 1 ohm in the exposed coil being 27.88 kilocalories per sq. ft. per hour. The chief source of error in calibration was the uncertainty of temperature of the surrounding air and walls of the room: the correction for difference between air and bolometer was 0.028 ohm per 1° C. and sometimes amounted to 4%, but the divergence of the corrected results from the mean was generally less than 0.5%. In testing a gas fire the bolometer was mounted on a revolving sector of fixed radius ( $\frac{9}{16}$  feet), the centre of which was adjusted to coincide with the centre of the fire; uncertainty as regards the position of the latter point was the chief source of error, a variation of 1 in. in the radius of the sector causing a difference of 6% in the central reading. A close approximation to the total radiation over a hemisphere at a distance, D, was obtained by multiplying the sum of the central reading and 4 readings taken at 60° along the equator and meridian by  $\frac{16}{3} D^2$ , the "distribution factor" of the fire being this product divided by the central reading. The method is more accurate, reliable, and rapid than the "Leeds method" (water radiometer and thermopile) hitherto employed, and may be made automatic if required.—W. E. F. P.

*Determination of the composition of argon-nitrogen mixtures (for filling half-watt lamps).* Hamburger and Filippo. See VII.

### PATENTS.

*Charcoal kiln.* A. R. Bellamy, Grantham, Eng. Pat. 5858, March 7, 1914.

THE body of a vertical cylindrical kiln, made in sections, is provided with air inlets controlled by hinged or sliding doors opening either directly into the kiln or into an annular passage communicating with the kiln. Grate bars carried by a frame fixed across the discharge opening in the conical bottom, may be partly withdrawn to vary the air supply. A horizontal door is hinged to the frame below the bars.—W. F. F.

*Carbon; Manufacture of a substance suitable for the production of pure* — Soc. des Combustibles Industriels, Fr. Pat. 472,082, July 24, 1913.

HYDROCARBONS such as tar, tar oil, petrol, or their derivatives, or other organic substances rich in



carbon and deficient in mineral matter which boil below 200° C., are filtered and subjected to the prolonged action of a current of air or oxidising gas while being heated to a temperature insufficient to cause coking. The mass thus obtained is treated with organic solvents and the insoluble portion carbonised. The soluble portion is heated to remove and recover the solvent, and the residue treated again.—W. F. F.

*Charcoal kiln.* J. M. Deschamps. Melbourne, Australia. Eng. Pat. 6536, March 14, 1914.

The kiln consists of a vertical, cylindrical steel shell lined with brick, the cover, which is hinged to and operated from a derrick or standard mounted upon the kiln, being provided with a sand seal. The air inlets at the side of the kiln are provided with valved tubes or sleeves to retard oxidation at the circumference of the charge; the tubes may be inserted to varying distances within the kiln to promote conversion of wood into charcoal towards the centre. The discharge of charcoal into a cooling tank, and the admission of air for combustion, are controlled by means of an adjustable door in the inverted conical casting forming the bottom of the kiln, and the brick lining is supported on a ring forming the top of the latter casting. Claim is also made for a portable apparatus of similar construction.—W. E. F. P.

*Flame-arc lamp and electrode therefor.* G. Egly, Assignor to Gebrüder Siemens und Co., Berlin. U.S. Pat. 1,132,313, March 16, 1915. Date of appl., Sept. 9, 1914.

The negative electrode contains a "slag-removing substance" such as an alkali carbonate, borate, etc., and the positive electrode the materials for producing luminosity.—W. E. F. P.

*Incandescence filaments of metallic tungsten or molybdenum for electric incandescence lamps; Manufacture of —.* A. Lederer. Atzgersdorf, Austria-Hungary. U.S. Pat. 1,132,523, March 16, 1915. Date of appl., Aug. 25, 1906.

SEE Eng. Pat. 18,738 of 1906; this J., 1907, 957.

### III.—TAR AND TAR PRODUCTS.

*Toluene recovery of Beckton.* J. Gas Lighting, March 30, 1915.

FOR some time past the Gas Light and Coke Co. has been treating daily 15 million cub. ft. of gas at Beckton for the recovery of toluene; the quantity will be increased shortly to 20 million cub. ft. Research and large-scale experimental work during the last two years have provided information as to the most suitable wash-oil and the quantity of oil required to extract a maximum quantity of toluol without materially reducing the illuminating power or calorific value of the gas. By using a limited amount of oil in the washers, very little benzene is extracted from the gas, and a crude spirit is obtained, rich in toluene, xylene, naphthalene, etc. By this means, only a small quantity of benzol has to be returned to the gas, and the plant for dealing with the saturated oil is small compared with that required when more wash-oil is used, and a greater proportion of the benzol is removed. Rotary and centrifugal washers are used for the absorption of the toluol by the wash-oil.

The method of working is as follows: The cooled debenzolised oil is pumped from the cold-oil store-tank at a constant rate through the washer, where it meets an opposing stream of gas. From the washer, the oil, now containing the

toluol, etc., runs into a store-tank, from which it is pumped through the counter-current heat economisers to the still, in which the wash-oil and the light spirit are separated by means of steam. This method of separation is not unduly expensive in steam, provided the wash-oil in the extraction washer is not used excessively. To secure further economy it is proposed to make a trial of a direct-heated coil, an expansion chamber being worked on the outlet. The hot wash-oil from the still flows to a collecting tank, from which it is pumped through the heat exchangers, and onwards through water-coolers, after which it flows to the store-tank, from which the extraction washer is fed. The light spirit vapours, after leaving the still, are conducted through a condenser, the condensed mixture of benzol and toluol flowing to a collecting tank after the separation of the condensed water. The mixture of spirit is afterwards rectified in a fractionating boiler, where the lighter spirit is separated from the toluol, xylol, etc., before this heavier boiling portion is sent to the products works for rectification—a yield of about  $\frac{1}{2}$  gall. of pure toluene per ton of coal carbonized being obtained.

#### PATENTS.

*Tar oils which may be used as paint oils and with increased antiseptic and fungicidal properties; Production of —.* Chem. Fabr. Dr. K. Albert and L. Berend. Fr. Pat. 471,671, April 6, 1914.

THE phenols in tar oils are condensed with formaldehyde, or with substances producing formaldehyde, to form resinous products; or resins formed from phenols and formaldehyde are dissolved in tar oils. Halogenated derivatives of the phenols may be employed. Compounds of lead, copper, and mercury may be added to increase the bactericidal properties, and siccatives may be added either before or after the condensation. The products may be used as paint oils, especially for submarine paints, and for impregnating wood.—F. S.

*2-Cyanoquinoline and 1-cyanoisquinoline; Preparation of —.* L. Givaudan, Vernier, u. A. Kaufmann. Ger. Pat. 280,973, June 20, 1913.

2-CYANOQUINOLINE, m. pt. 94° C., is obtained from 1-benzoyl-2-cyano-1,2-dihydroquinoline, and 1-cyanoisquinoline, m. pt. 78° C., from 2-benzoyl-1-cyano-1,2-dihydroisquinoline by treatment with phosphorus pentachloride, sulphuryl chloride, or thionyl chloride in presence of an anhydrous inert diluent. The products may be used for the preparation of dyestuffs and pharmaceutical chemicals.—A. S.

*Manufacture of antiseptics, disinfectants, and germicides [from peat tar].* Eng. Pat. 19,253. See XIXB.

### IV.—COLOURING MATTERS AND DYES.

*Indigo and other vat dyestuffs; Catalytic reduction of —.* A. Brochet. Comptes rend., 1915, 160, 306—308.

THE catalytic hydrogenation of liquids in presence of common metals (this J., 1914, 612, 1113) has been extended to the reduction of solids suspended in water. 10 grms. of Indigo was suspended in 250 c.c. of water to which had been added 10 c.c. of caustic soda solution, and 5 grms. of active nickel was added in an atmosphere of hydrogen, using the glass apparatus described previously. The reaction proceeded most rapidly at 60°–80° C., giving the greenish yellow solution of Indigo White.

At the end of 40 mins. shaking at 70° C., 910 c.c. of hydrogen (measured over water at 15° C.) had been absorbed. The nickel was separated by filtration. The liquid obtained did not contain an excess of reducing agent, as is the case when hydro-sulphite is used. If necessary more than the above amount of Indigo may be used in suspension; the paste is reduced more rapidly than the powder. The process may be used for obtaining Indigo White as a concentrated solution or paste. A lime or neutral vat may be used, the reaction being much slower in the latter case. The activity of the nickel is of the same order after standing under water for one year.—F. W. A.

*Fustic from Jamaica and British Honduras for khaki dyeing.* Chem. Trade J., April 10, 1913.

THE present shortage in this country of synthetic yellow dyes has put considerable difficulties in the way of manufacturers of khaki cloth. A temporary expedient was found, however, by the increased use of fustic, a natural yellow dyestuff, consisting of the wood of a tree (*Chlorophora tinctoria*), which grows freely in Jamaica and also in British Honduras. The increased demand has now greatly raised the price of fustic, of which at the outbreak of the war there was only a small supply available in Europe, though one of the prizes captured from Germany had a considerable consignment on board. A certain amount, too, has been obtained from France, which country and the United States have hitherto taken the bulk of the fustic exported from Jamaica.

When the shortage of yellow dyestuffs in this country first became apparent, the Imperial Institute took steps to place British dye firms in touch with exporters of fustic in Jamaica. Only a moderate amount of cut fustic wood was then available in the island, but, as a result of the Institute's action, the Government of Jamaica have offered to purchase from the growers further supplies and carry these at Government cost to Kingston, the port of shipment. Negotiations are accordingly now pending for the purchase and shipment of considerable quantities of Jamaica fustic by dyers in this country. The Government of British Honduras is also taking action in this matter, and a further supply of the wood may possibly be forthcoming from that Colony. Further information may be obtained on application to the Imperial Institute, South Kensington, London, S.W.

#### PATENTS.

*Monoazo dyestuffs; Manufacture of new*—Farbenfabr. vorm. F. Bayer und Co. Second Addition, dated April 21, 1914, to Fr. Pat. 457,840, April 21, 1913 (see this J., 1913, 1004; 1914, 414). Under Int. Conv., May 2, 1913.

Is place of aminoacylamino-salicylic acids, amino-acyl-*o*-aminophenols or their derivatives or substitution products may be diazotised and combined with pyrazolones or with  $\alpha$ -methylindole.—F. W. A.

*Azo dyestuffs; Manufacture of yellow*—Farbenfabr. vorm. F. Bayer und Co. Fr. Pat. 471,850, May 5, 1914. Under Int. Conv., May 8 and 15, 1913.

ACYLATED aminothiazoles of the benzene series containing at least one methyl group attached to the benzene nucleus are oxidised with permanganate in neutral or alkaline solution, and if desired the acyl group is eliminated from the products. The resulting aminothiazolecarboxylic acids are diazotised and combined with aceto-acetic arylides; the products give yellow shades on cotton.—F. W. A.

*Dyestuffs; Manufacture of new intermediate products and their conversion into*—Soc. pour l'Ind. Chim. à Bâle. Fr. Pat. 471,853, July 16, 1913.

A NEW series of chlorimides has been obtained by the action of hypochlorite or of chlorine on arylsulphoarylene-*p*-diamines of the type, (2)NH<sub>2</sub>.R.NH.SO<sub>2</sub>.Ar(1), in which R is an arylene residue of the benzene or naphthalene series. The arylsulphiminoarylenechlorimides obtained, CLN:R:N.SO<sub>2</sub>.Ar, may be condensed with amines, phenols, naphthols, and especially with carbazole or its derivatives, to give products which may be used in the preparation of sulphide or sulphurised vat dyestuffs.—F. W. A.

*Azo dyestuffs; Manufacture of chrome*—Soc. pour l'Ind. Chim. à Bâle. Fr. Pat. 471,898, July 17, 1913.

MONOAZO dyestuffs, obtained by combining diazotised sulphonated *o*-aminophenols or *o*-aminonaphthols or their derivatives with *m*-aminophenols in alkaline solution, are diazotised and combined with suitable compounds to obtain dyestuffs which may be after-chromed.—F. W. A.

*Vat dyestuffs; Manufacture of new*—Soc. pour l'Ind. Chim. à Bâle. Fr. Pat. 471,776, July 18, 1913.

Ox treatment with oxidising agents (nitric acid, manganese dioxide, lead dioxide, per-salts, etc.) in acid solution, indigo and indigoid dyestuffs give vat dyestuffs which in most cases possess greater fastness and also greater affinity for cotton than the original dyestuff. Halogenation of the products leads to the production of other vat dyestuffs.—F. W. A.

*Vat dyestuffs derived from indophenols; Manufacture of*—Soc. pour l'Ind. Chim. à Bâle. Fr. Pat. 472,087, July 25, 1913.

Ox treatment with warm dilute solutions of alkali or alkaline-earth sulphides, indophenols give vat dyestuffs which, unlike the original indophenols, are fast to acids and to light. For dyeing, 1 part of dyestuff is mixed with 3 parts of caustic soda, 30–40 parts of water and then 2–3 parts of sodium hydrosulphite added, and the liquid heated to 80° C. until solution is complete. After dilution, wool is dyed in the bath at 50°–60° C. for half-an-hour, exposed to air for an hour, rinsed and dried. The material is then immersed for half-an-hour at 70°–80° C., in a bath containing 3–4 grms. of potassium bichromate, or copper or nickel sulphate, and 2.5 c.c. of acetic acid per litre.—F. W. A.

*Arylaminoanthraquinones; Manufacture of derivatives of*—Farbw. vorm. Meister, Lucius, und Brünig. Fr. Pat. 472,100, May 11, 1914. Under Int. Conv., May 22 and Dec. 8, 1913, and Feb. 20, 1914.

NITRO or halogen derivatives of oxazoles, obtained from  $\beta$ -aminoalizarin and aromatic acids, are treated with primary aromatic amines, and the products sulphonated in the usual manner. The oxazoles may be replaced by their sulphonic acids, or by other heterocyclic derivatives of  $\beta$ -aminoalizarin. The sulphonic acids obtained possess a very high tinctorial power, dyeing wool fast violet shades which become green on chroming. The dyeings are very fast to potting, light, and washing.—F. W. A.

### V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

*Arundo Donax* for paper making. J. Beveridge. Paper Making, 1915, 34, 88—90.

THE *Arundo Donax* cane, a native of S. Africa, grows in swampy ground and in a season attains a height of 18—20 ft. with a diameter of 1—1.5 in. When mature, it has a pale golden colour and clean, glossy, silicious surface. It should be cut before it is fully mature and crushed between rollers immediately after cutting. When digested with bisulphite liquor prepared from a magnesia base, with 3.74% total  $\text{SO}_2$ , of which 66% was "free," this cane presented no difficulty and yielded under conditions similar to those employed for spruce wood, 32.2% of air-dry fibre, which could be bleached to a pure white with 10.4% of bleaching powder. By the caustic soda process, it required 24.1%  $\text{Na}_2\text{O}$  as caustic to effect a satisfactory digestion under a steam pressure of 90 lb. per sq. in. maintained for 5 hours. The yield was 33.1% of air-dry pulp which could be bleached with 13.6% of bleaching powder. The sulphite process would appear to be more economical. The fibre is long, soft, and silky and is described as superior to those of megasse and bamboo; the pulp contains less non-fibrous cellular matter than either of these and resembles the pulps obtained from coniferous woods in uniformity, though not in strength.

—J. F. B.

*Ledger stock; The sizing of high-grade* —. H. A. Maddox. Paper Making, 1915, 34, 75—80.

THE usual tests for the quality of gelatin intended for tub-sizing are described. The strength of the sizing solution is varied according to the condition of the paper and the preliminary engine-sizing, if any; an average concentration is about 5% of gelatin. Damp paper absorbs gelatin size more readily than dry, but the absorption may be irregular, giving a blotchy appearance when viewed by transmitted light. The penetration of the size is largely dependent on the viscosity of the solution. The viscosity of the size may be diminished and the penetration improved by increasing the temperature, but the sizing efficiency is diminished. The proportion of alum added to the pulp when the paper is made is of great importance; an excess of alum gradually destroys the ultramarine colouring matter, and opposes the thorough penetration of the size by its coagulating action, whereby the size remains mostly on the surface. The air imprisoned in the paper likewise opposes uniform penetration and its escape later, in the drying process, may disturb the regularity of the sized surface. An excessive temperature in drying is very prejudicial to effective sizing. A serious drawback of hard tub-sized ledger papers, particularly hand-made papers, is the resistance offered to writing with fountain pens which lack the sharpness or roughness necessary to scratch the horny surface; similarly this hard surface causes abnormal wear on the pens of the account-book ruling machines.—J. F. B.

*Paper; Chemical analysis of* —. H. A. Bromley. Chem. News, 1915, 111, 136—140.

CHEMICAL methods may be used to determine fibrous composition in the case of esparto pulp (yield of fural) and mechanical wood pulp. The usual loadings consist of calcium sulphate, barium sulphate, china clay, and talc, the various constituents of which are determined by an analysis of the ash. The nitrogenous constituents of paper are preferably determined by Kjeldahl's method; the factor for dry gelatin is 5.56 and for casein 4.90. Sammet's method (this J., 1913, 939)

is preferred for the determination of rosin. Starch is determined after conversion either by malt extract or by acid, the products being estimated by Fehling's solution. Colouring matters which leave characteristic compounds after incineration are estimated by an analysis of the ash; in the case of ultramarine, the composition of which is indefinite, the colour of the ash may be matched against standard mixtures of ultramarine and china clay. Salicylic acid, when present as a preservative, may be extracted with light petroleum spirit and after diluting the extract with an equal volume of 95% alcohol, may be titrated with  $N/10$  alkali, using phenolphthalein as indicator. For the estimation of carboic acid in paper, the bromine absorption method is useless; the author prefers a method based on Muter's process, in which the paper is extracted with alcohol and the extract evaporated with caustic soda; tar oils and naphthalene are removed by filtration, and the phenols liberated with acid and extracted with ether or light petroleum. Arsenic in fly-papers may be extracted by boiling with sodium bicarbonate, and the extract titrated with  $N/10$  iodine.—J. F. B.

*Waste products of agricultural interest—wool and leather wastes.* Russell. See XVI.

#### PATENTS.

*Wool; Washing and bleaching of* — and recovery of the grease, potassium salts, and the reagents employed. R. Vidal. Fr. Pat. 471,654, July 16, 1913.

Raw wool is washed with a 5—10% solution of a sulphite or bisulphite of an alkali or alkaline earth; the solution recovered contains the potassium salts extracted from the wool, which are converted into sulphite by treating the liquor with sulphur dioxide. The material is next treated with a solution or emulsion of hydrocarbons or chloro derivatives of hydrocarbons in solutions of castor oil or other soap, the bath containing 3—5% of the organic solvent. When this bath becomes saturated, the grease and volatile solvent are recovered by skimming, acidification, or other means.—J. F. B.

*Silk; Process of making a felted mass of* —. G. Diesser. Fr. Pat. 472,351, May 19, 1914. Under Int. Conv., May 20, 1913.

DEGUMMED silk waste is treated with formic acid, either as liquid or vapour, at the ordinary temperature, until the fibres are gelatinised and partially dissolved. The excess of acid is removed and the felted mass dried.—J. F. B.

*Plastic material; Manufacture of* —. P. Cassier. Fr. Pat. 471,390, July 8, 1913.

MECHANICAL wood pulp or other material containing cellulose is kneaded with dilute sulphuric acid (2 parts of acid of 66° B., sp. gr. 1.84, to 1 of water) until gelatinised. The mass is pressed, washed, and moulded or worked into the required shapes. The product is non-inflammable and a good electrical insulator.—F. Sp.

*Threads, films, gauze, etc.; Manufacture of* — from cellulose. C. Shrager and R. D. Lance. Fr. Pat. 471,471, July 10, 1913.

CELLULOSE is treated with a mixture of equal volumes of water and a strong acid, e.g., sulphuric acid of 66° B. (sp. gr. 1.84). It is then freed from acid, and treated with carbon bisulphide. After removing the excess of the latter, the mixture is dissolved in caustic soda and converted into threads or films by precipitation in an acid bath, which may contain 30% of sulphuric acid, with or without

sodium sulphate or bisulphate. If the water in the preliminary treatment is replaced by acetic acid of 8° B. (sp. gr. 1.06), the cellulose dissolves. It may then either be spun into an alkaline coagulating solution or be coagulated by ammonia and redissolved in caustic soda solution. Resin may be incorporated in the final product by the addition of resins to the caustic soda solution of depolymerised cellulose, and it may be combined in the product as resins by addition of salts of metals (e.g., zinc, magnesium, aluminium) to the precipitating bath and subsequent treatment of the coagulated threads with a faintly alkaline bath. The use of aluminium salts facilitates subsequent drying of the product.—F. Sp.

*Celluloid and other cellulose products; Production of permanent iridescent effects on* —. E. Heusch and J. Paisscau. Fr. Pat. 471,581, July 15, 1913.

IRIDESCENT effects are produced by coating objects with a solution of a cellulose ester to which have been added dyes, pigments, bronze powder, fish scales, etc., and the iridescent surface is protected by coating it with a transparent substance, such as a different cellulose ester, which resists water, the solvents being such as do not dissolve the iridescent coating.—F. Sp.

*Wood and other vegetable substances; Process and apparatus for making cellulose from* — and extracting resinous, oily and other constituents. W. K. Freeman. Fr. Pat. 471,620, Dec. 18, 1913.

THE chips of wood are digested, in an atmosphere of hydrogen, with alkaline solutions in three separate stages, first with a solution of low alkaline strength to extract gums, resins, and volatile oils, next with a strong solution to effect the complete digestion of the tissues, and lastly with a fresh dilute solution to cleanse the pulp produced in the second stage, this last liquor being used again for the first stage of the next operation. The apparatus consists of a digester, a circulating pump, a series of settling vessels for the accumulation of the heavy by-products and the separate storage of the various digesting solutions, an oil-separating chamber, and one or two condensers, all forming a closed circuit.—J. F. B.

*Half-stuff from wood; Manufacture of* —. E. Bergerhoff. Ger. Pat. 279,411, Jan. 11, 1914.

THE wood is boiled with sulphite liquor and then, whilst still tolerably hard and maintaining its original form, is removed from the boiler and ground to pulp in an edge runner. The quantity of sulphite liquor used is such that the residual liquor contains sufficient sulphurous acid to be used for treating another charge of wood.—A. S.

*Pulp from red beech wood; Production of pale-coloured, easy-bleaching* —. C. Braun. Ger. Pat. 279,517, June 17, 1913.

THE wood is boiled under pressure with a mixture of calcium bisulphite and alkali sulphite or magnesium sulphite, containing only 40–50% of "free" SO<sub>2</sub>, and after removing the liquor, the pulp is washed in the boiler, with exclusion of air, first with hot and then with cold water containing a small quantity of sulphurous acid. The yield of pulp is 43–45% of the air-dry wood, and the product can be bleached with 8–9% of bleaching powder. (See also Ger. Pat. 261,848; this J., 1913, 823.)—A. S.

*Fibrous material [paper] in layers for chemical and electrical purposes; Manufacture of* —. Meirowsky and Co. Akt.-Ges. Fr. Pat. 471,836, May 5, 1914.

FIBROUS material, e.g., paper in sheets or webs, is impregnated with a small proportion of oil and

coated with a natural or synthetic resinous material. The several layers are then united by the application of heat and pressure.—J. F. B.

*Sulphite liquor; Process of treating waste* —. M. W. Hedden, Oregon City, Oreg. U.S. Pat. 1,130,817, March 9, 1915. Date of appl., Dec. 12, 1914.

NEUTRALISED waste sulphite liquor is digested with a cyanogen compound to remove all the sulphur-bearing groups and then saturated with sodium chloride or an electrolyte other than a mineral acid to precipitate organic cyanogen compounds.—J. F. B.

*Plants; Method for opening out* — or loosening their fibres. C. F. Kübler, Wilmersdorf, Germany. U.S. Pat. 1,131,715, March 16, 1915. Date of appl., Nov. 9, 1912.

SEE Eng. Pat. 25,680 of 1912; this J., 1913, 747.

*Sulphite cellulose; Process of producing* —. E. Oman, Stockholm. U.S. Pat. 1,130,192, March 2, 1915. Date of appl., Jan. 19, 1914.

SEE Eng. Pat. 1145 of 1914; this J., 1914, 348.

*Artificial silk threads or similar products; Process for precipitating copper-ammonia solutions of cellulose for the purpose of manufacturing* —. E. G. Legrand, St. Adresse, France. U.S. Pat. 1,130,830, March 9, 1915. Date of appl., Aug. 29, 1912.

SEE Ger. Pat. 250,357 of 1911; this J., 1912, 1120.

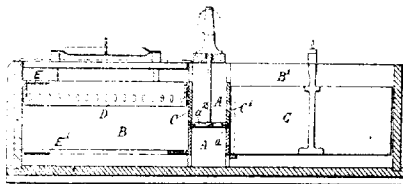
## VI.—BLEACHING; DYEING; PRINTING; FINISHING.

*Indigo and other vat dyestuffs; Catalytic reduction of* —. Brochet. See IV.

### PATENTS.

*Dyeing machines.* A. R. Whitehead, Leeds, and J. Farrar, Halifax. Eng. Pat. 5569, March 5, 1914.

A CIRCULATING chamber, A, contains two propellers, *a*<sup>2</sup>, which fit into circular openings in the horizontal partition, *a*. The division boards,



C and C<sup>1</sup>, may be mounted in slides and so arranged that the dye liquor circulates in either or both the dye-vats, B and B<sup>1</sup>, in a direction determined by the propellers. In the case shown, the vat, B, contains a rack, D, for hanks with circulating sticks, E and E<sup>1</sup>, and the vat, B<sup>1</sup>, contains a cage, G, for loose wool or balls of wool.—F. W. A.

*Dyeing process.* A. J. Rau, Clifton, N.J. U.S. Pat. 1,131,083, March 9, 1915. Date of appl., March 4, 1911.

THE fabric is wrapped in layers or coils and the dye liquor forced through the layers. The order

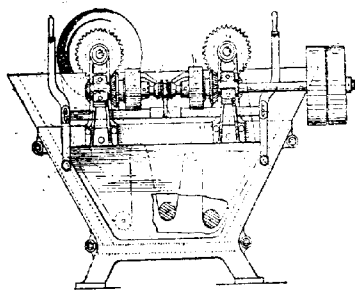
of the layers or the coil is then reversed, and the dye liquor forced through in the opposite direction.—F. W. A.

**Dyeing apparatus.** A. J. and J. A. Rau, Clifton, N.J. U.S. Pat. 1,131,084, March 9, 1915. Date of appl., March 11, 1914.

AN apparatus for carrying out the process described in the preceding abstract. Two drums rotating in the dye-bath are used, the fabric being unrolled from one and wound on to the other, so that opposite surfaces of the fabric are presented to the drums in succession.—F. W. A.

**Jigger for dyeing fabrics and similar purposes.** H. L. Quick, New York. U.S. Pat. 1,131,269, March 9, 1915. Date of appl., Jan. 7, 1914.

THE jigger is fitted with gears, for operating the shafts driving the revolving rollers, which are mounted independently of these shafts and of the



rollers. Flexible connections are provided for connecting the gears mounted on bearing sleeves to the shafts, and clutches for independently disconnecting gears from the shafts.—F. W. A.

**Fabrics; Method of treating**—[with dye liquor, etc.]. H. L. Quick, New York, N.Y. U.S. Pat. 1,131,270, March 9, 1915. Date of appl., Jan. 7, 1914.

THE liquor with which the fabric is to be treated is placed in the interior of a tight roll of the fabric, and the roll rotated to force the liquor through by centrifugal force. The fabric may be wound in layers on a perforated shell to form the roll.—F. W. A.

**Multicolour designs; Production of**—[and of "shadow" designs]. I. Orloff. Fr. Pat. 472,092, July 26, 1913.

THE effects of the non-registering of the rollers in printing multicolour designs are avoided by making the impressions of the second multicolour design overlap the impression from the principal roller. In case these impressions are geometrically similar, the illusion of shadow is obtained. The complete design is printed in one operation, the printed colours meeting on the fabric in a moist condition.—F. W. A.

**Waterproofing of fabrics, yarns, and other materials.** A. M. Hart, Assignor to Viking Manufacturing Co., Ltd., London. U.S. Pat. 1,131,929, March 16, 1915. Date of appl., Aug. 4, 1911.

SEE Eng. Pat. 18,607 of 1910; this J., 1911, 1448.

**Satinising cotton fabrics; Process of**—, H. Duttschke, Elberfeld, Germany. U.S. Pat. 1,132,001, March 16, 1915. Date of appl., Feb. 10, 1914.

SEE Fr. Pat. 467,670 of 1914; this J., 1914, 860.

**Washing and bleaching of wool and recovery of grease and potassium salts.** Fr. Pat. 471,654. See V.

## VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

**Indian chemical industries. A retrospect.** P. G. Shah. Paper read before the Indian Industrial Conference, Madras, Dec., 1914.

THE Indian chemical manufactures, which have been confined to the small scale production of such materials as saltpetre, sulphuric acid, alum, borax, alkali salts, and ammonium compounds, show great possibilities of development. Local conditions, however, in many respects favour small scale production and militate against the establishment of large factories. At present, owing partly to the undeveloped state of other Indian industries, local resources are very incompletely utilised in chemical manufactures. The growing demand for chemicals is evidenced by the following figures showing the annual value of imported chemicals in lakhs of rupees: 1876, 0.98; 1895, 4.6; 1904, 29.7; 1911, 96.4; 1912, 93.2; 1913, 101.4. The 1912 figures include sulphuric acid 3.7, sulphates of alumina 4.6, calcium carbide 1.5, disinfectants 3.8, potassium cyanide 3.7, sodium bicarbonate 4.2, sodium carbonate 11.1, caustic soda 8.0, sulphur 5.3, and ammonium compounds 3.75 lakhs. Compared with the rising imports, the exports of chemicals are insignificant and partly declining. The value of exported chemicals (92% of which was saltpetre), drugs, and tanning materials for 1912 amounted to 36.6, 20.7, and 104.0 lakhs, respectively. On the whole, raw materials are abundant, but skilled labour is difficult to obtain. Numerous small pharmaceutical works have recently been started throughout the country, in addition to a few larger factories, such as the Bengal Chemical Works (Calcutta), the Alembic Chemical Works (Baroda), the Pioneer Alkali Works (Bombay), the Gujarat Chemical Works (Ahmedabad), and the Eastern Chemical Works (Bombay); but owing to the rapidly increasing demand for chemicals these works have not caused any diminution in chemical imports. There is an extensive demand for chemicals used in the sizing, bleaching, and dyeing of cotton goods. Saltpetre is obtained chiefly from the Gaya, Tirhoot, Saran, and Champaran districts of Behar, which have an agricultural population of over 500 per square mile. The effloresced earth is boiled with water and the sodium chloride and potassium nitrate roughly separated by fractional crystallisation. There are 40,000 factories and 600 refineries engaged in this work, the latter employing 50,000 hands. The methods are rather wasteful and capable of improvement. The present annual production of the refined material averages about 25,000 tons, of which 15,000 tons valued at 40 lakhs are exported, chiefly from Calcutta, to Hongkong (32%), U.S.A. (23%), and the United Kingdom (20%). It is suggested that the product should be utilised in local chemical manufactures rather than exported. The annual Indian consumption of sulphuric acid is below 10,000 tons. Sulphuric acid is made by the Government Cordite Factory (Nilgiris), Messrs. Waldie and Co. (Calcutta and Cawnpore), Messrs. Perry and Co. (Madras), the Burma Chemical Industries Co. (Rangoon), the Bengal Chemical and Pharmaceutical Works, Ltd. (Calcutta), and by several smaller works, from Sicilian and Japanese sulphur and Indian saltpetre. No workable deposit of sulphur or iron pyrites has yet been

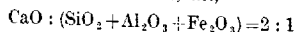
located in the country. The amount of imported acid fell from 79,772 cwt. in 1910 to 38,780 cwt. in 1912, while the amount of imported sulphur rose from 104,301 cwt. in 1911 to 114,498 cwt. in 1912. The cheapness of saltpetre renders Gay Lussac and Glover towers unnecessary, and the high sea and railway freights act as a protection to the industry; the cost of the acid in India is about ten times the English price. Lack of cheap sulphuric acid has been largely responsible for the annual importation of over £20,000,000 worth of products manufactured in Europe from minerals which are obtainable in India. Potassium carbonate is prepared solely from wood ashes, though Indian saltpetre might be utilised for this purpose. In 1913 the imported potassium salts, apart from potassium cyanide, reached a value of 2.25 lakhs. Sodium carbonate occurs in appreciable quantities in the Reh efflorescence and it is also obtained from calcined seaweed (barilla) and from certain lake-waters. Washing soda is manufactured by the Pioneer Alkali Works from partly imported material. Sodium salts of the value of £70,000 were imported in 1904, and £183,822 in 1912. In 1912, 11,633 cwt. of ammonium compounds, valued at £25,403, was imported, but ammonium chloride is now being made from ammoniacal gas-liquor at Bombay. Ammonium sulphate has not been made to any appreciable extent, and in the "coking" operations in the Bengal coalfield the annual wastage of nitrogen has been equivalent to ammonium sulphate of the value of 20 lakhs of rupees; recovery plants are now being introduced. The imports of chemical manures rose from £2040 in 1907 to £42,592 in 1912; in the same years the value of exported bones rose from £363,002 to £525,739, the price of sulphuric acid being here again a decisive factor. Soda alum is made in Behar and other localities by adding soil scrapings to the aqueous extract from roasted pyritous shale; the product is practically wholly utilised in the Indian tanning and dyeing industries: in spite of the abundance of aluminous clays and laterite the production is declining, and in 1912, 101,088 cwt. of sulphates of alumina (including alum) valued at £31,146 was imported. The so-called Indian borax is largely imported from Kashmir and Tibet and is used as a mordant, antiseptic, insecticide, glazing material, etc.; in 1912, the exports, which are declining, amounted to 4770 cwt. valued at 111,869 rupees, and the imports from Great Britain to 6688 cwt. valued at £6144. Among the problems awaiting investigation are the effective utilisation of the crude saltpetre and saltpetre refuse, of the Reh efflorescence, and of the large deposits of laterite and clays; the purification of the magnesium compounds which accumulate in the extensive manufacture of salt from seawater; and the efficient separation of magnesium and potassium salts from the Punjab rock-salt. (Note: Lakh=100,000 rupees=£6066).—J.R.

*Selenic and telluric acids and their salts; Reactions of —.* G. Deniges. Ann. Chim. Analyt., 1915, 20, 57—59.

WHEN a solution containing selenic acid or its salts is mixed with one-half its volume of a solution of 10 gms. of mercurous nitrate in a mixture of 10 c.c. of nitric acid (sp. gr. 1.39) and 100 c.c. of water, a white precipitate of mercurous selenate is formed; this precipitate rapidly becomes crystalline and the crystals exhibit a characteristic form when examined microscopically. Selenous acid also yields characteristic crystals of mercurous selenite when treated with the reagent. Telluric acid or a tellurate yields a yellow crystalline precipitate of mercurous tellurate.—W. P. S.

*Potash extraction from felspar, etc., in cement-burning; Jungner's method of —.* Stein u. Cement, 1914. Chem.-Zeit., 1915, 39, Rep. 63.

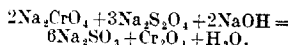
RAPID and complete volatilisation of potassium and sodium oxides occurs when a mixture of felspar and lime is heated to 1400°—1450° C. The most suitable proportion is that employed in the manufacture of cement, i.e.,



or 1 part of felspar to 3 parts of calcium carbonate; the process effects a clean separation of cement and alkali. A mineral containing 12% K<sub>2</sub>O gave a residual cement clinker containing only 0.05% K<sub>2</sub>O, and cement prepared from the so-called "röd fyr" contained 0.07% K<sub>2</sub>O after burning for only 20 mins. The total amount soluble in acid was 0.21% for the latter cement, 0.26% for a cement made from a gneiss rich in potash, and 0.15% for a felspar cement. Upon applying the Jungner method to the ordinary process of cement manufacture the volatilised potassium oxide is converted into potassium carbonate by the combustion gases and condenses as a fine white powder. At very little extra cost a rotary cement kiln with an annual capacity of 4000 metric tons of clinker could be utilised to produce simultaneously 1600 metric tons of potash (K<sub>2</sub>O); the total annual production of thirty to forty million metric tons of cement, if obtained from a mineral of medium potash content, would correspond to an accompanying production of one million metric tons of potash. (See Eng. Pats. 26,497 and 28,970 of 1912; this J., 1913, 486, 534.—J. R.

*Hydrosulphites; New method of valuing —.* E. Knecht. J. Soc. Dyers and Col., 1915, 31, 94—96.

HYDROSULPHITES are oxidised quantitatively to sulphites by alkaline solutions of chromates,



whereas sulphites are without action on such solutions: 0.1—0.2 gm. of commercial solid hydrosulphite is added to 20 c.c. of N/10 potassium bichromate which has been made alkaline with an excess of caustic soda, the solution is boiled for 4—5 minutes, the precipitated chromium hydroxide is separated and boiled with water and sodium peroxide until it has dissolved and the excess of sodium peroxide has been destroyed. The solution is acidulated with sulphuric acid, and the chromium estimated by adding an excess of standardised titanous chloride and titrating back with iron alum, or by the ordinary ferrous sulphate method. —F. W. A.

*Silver chloride; Solubility of —.* Z. Glowczynski. Kolloidchem. Beihette, 1914, 4, 147—176. Z. angew. Chem., 1914, 27, Ref., 721.

THE high values for the solubility of silver chloride found by Stas were probably due to the fact that his specimens contained substances which exerted a specific action on the solubility. The solubility of precipitated silver chloride increases considerably with its degree of dispersion. Precipitates produced by a concentrated solution of potassium chloride show varying solubility according to the conditions of precipitation, but with a dilute solution of potassium chloride, constant values are obtained. Silver chloride is less soluble in very dilute solutions of potassium chloride and ammonium chloride than in water, but the values are considerably higher than corresponds with the law of mass action. The solubility is increased by nitric acid.—A. S.

*Mercuric cyanide; Action of metals upon [and detection and determination of]—* C. Pertusi. Chem.-Zeit., 1914, 38, 1203—1204.

MERCURY is partially displaced from mercuric cyanide by magnesium, zinc, aluminium, and other metals. The calculated amount of magnesium displaced 40% of the mercury after 24 hours, and by using ten times this amount of magnesium, 92—94% of the mercury was displaced. By passing carbon dioxide or by boiling, the reaction attained completion in half an hour; a similar result was achieved by passing hydrogen for 1½ to 2 hours. The resulting solutions contained CN<sup>-</sup> ions and were usually alkaline. The reaction failed with iron, nickel, and tin, but was given by lead, antimony, and bismuth. For qualitative work carbon dioxide was slowly passed through the solution to which had been added a little magnesium or antimony powder, two drops of copper acetate, and one drop of benzidine acetate. A sky-blue precipitate after not more than a minute indicated the presence of CN<sup>-</sup>. A distinct colour was given by 0.00005 gm. of mercuric cyanide in 10 c.c. In the presence of iodate or periodate it was necessary to add a little saturated baryta water before testing. For quantitative work hydrogen was passed slowly into a flask containing the solution of mercuric cyanide (0.5 gm.) in distilled water (40 c.c.) to which magnesium powder (0.6 gm.) had been added. The gas issued into a second flask graduated from 100 to 110 c.c. and containing about 30 c.c. of N/1 potassium hydroxide. After two hours the contents of the first flask were transferred to the second, washing being accomplished with alkaline water. The mixture was made up to 110 c.c. and the cyanide estimated in 100 c.c. of the filtered solution. The mean of five experiments gave 21.35% HCN instead of 21.46%.—J. R.

*Ferric oxide; Hydrous—* W. D. Bancroft. J. Phys. Chem., 1915, 19, 232—240.

THE properties of ferric oxide are affected by its water content and the size of the particles, and an indefinite number of distinct colloidal solutions of the hydrous oxide may be prepared. Graham's highly hydrous form, prepared by dialysing cold ferric acetate solution, is gelatinous and changes slowly into less hydrous forms; it is not homogeneous since it yields both limonite and hematite on heating. The oxide obtained by Péan de St. Gilles by boiling a dilute solution of ferric acetate, is sandy and less hydrous than Graham's modification; the particles are also coarser (about 7  $\mu$ ), but they coalesce less readily and are peptonised more readily after precipitation by hydrochloric or nitric acids. Various salts and acids readily precipitate the Péan de St. Gilles oxide in a gelatinous and more hydrous form.—J. R.

*Copper sulphate; New method for the technical preparation of—* P. Falcicola. Annali Chim. Appl., 1915, 3, 80—95.

A HOT mixture of sulphur dioxide and air, e.g., the gas from sulphur or pyrites burners, is passed upwards through a glass tower surrounded by a hot-air jacket and packed with copper turnings or shot, and nitric acid or nitrous gases are introduced at the upper part of the tower. Copper sulphate free from nitrate has been obtained in this way in laboratory experiments, and it is suggested that towers packed with copper might be used in place of Glover towers in the manufacture of sulphuric acid by the chamber process.—A. S.

*Zinc and manganese; Precipitation of— by ammonium sulphide.* F. Seeligman. Z. anal. Chem., 1915. Pharm. J., 1915, 94, 389.

THE precipitation of manganese, but not of zinc, by ammonium sulphide is hindered by the presence

of ammonium salts unless a few drops of hydrogen peroxide solution are added.—T. C.

*Nitrogen; A chemically active modification of—, produced by the electric discharge.* VI. R. J. Strutt. Proc. Roy. Soc., 1915, A, 91, 303—318. (See also this J., 1914, 548.)

THE very small yield of active nitrogen obtainable from perfectly pure nitrogen is very largely increased by the presence of about 1/1000 part of almost any foreign gas (not necessarily containing oxygen), the increase due to the addition of 1/30,000 part of methane being particularly noticeable. It is suggested that the impurity (catalyst) acts by loading the electrons in the discharge and thus altering the character of their impact with the nitrogen molecules, this view being supported by the fact that gases containing oxygen, sulphur, chlorine, carbon, or hydrogen (atoms capable of attaching themselves to electrons in the discharge) promote, whereas argon, helium, and nitrogen itself (atoms incapable of loading electrons) do not promote the formation of active nitrogen. A nitride was produced when active nitrogen was shaken with cold, liquid mercury, but no development of mercury spectrum occurred as during the combination of active nitrogen with mercury vapour; similar results were obtained with other melted metals. The colour of a weak solution of indigo in sulphuric acid was slowly discharged when active nitrogen was bubbled through the liquid. Active nitrogen was found to react freely with pure pentane and heptane, and to a less extent with pure methane, producing hydrocyanic acid. —W. E. F. P.

*German Potash Syndicate.* Brit. and Col. Drug., April 9, 1915.

AS a result of the bringing into operation of numerous new potash mines during the past few years, the number of members of the German Potash Syndicate has gradually been increased from 40 or 50 to close upon 200 at the present time. The recent imposition of a veto on the export trade, combined with a scarcity of rolling stock in the inland market, has produced chaos in the industry, and the turnover of the syndicate, which in December, 1914, had again risen so far as to reach the level of the deliveries in the corresponding month in 1913, only amounted to the value of £1,300,000 in January and February, as contrasted with £2,450,000 in the corresponding months in 1914. The cost of production has increased largely, and many mines are only able to effect delivery at a large loss.

*Thorium content of the earth's crust; The average—* J. H. J. Poole. Phil. Mag., 1915, 29, 483—489.

THE thorium content of a large number of rocks and rock mixtures was determined by Joly's method, the material being fused with alkali carbonate at 1000° C., the product extracted with water, the residue dissolved in dilute hydrochloric acid, and after setting aside for some days for the thorium disintegration products to develop, the thorium determined by boiling off the emanation in a constant stream of air, which was then passed through an electroscope, and the rate of discharge compared with that produced when a thorianite solution of known strength was treated in a similar way. The solutions were boiled, before being tested, to expel any radium emanation present. The presence or absence of silica in the solutions, and actual manipulative details in the treatment of the rock, had no influence on the final results, and the activity after the first few days remained constant. The results showed that the thorium

content varied from  $2.3 \times 10^{-5}$  gm. per gram in acid rocks to  $0.22 \times 10^{-5}$ — $0.84 \times 10^{-5}$  gm. in basalts. On the assumption that the lithosphere approximates in composition to that of a diorite or intermediate rock, the average thorium content would be about  $1.6 \times 10^{-5}$  gm. per gram. From the values obtained for 86 acid, 48 intermediate, and 56 basic rocks, the arithmetic mean values are 2.13, 1.50, and  $0.51 \times 10^{-5}$  respectively. The ratio of radium to thorium increases in passing from acid to basic rocks.—G. F. M.

*Radium elements; Adsorption investigations with* —. K. Horowitz and F. Paneth. *Chem. Zeit.*, 1914, 38, 1206. (See also this J., 1914, 22; 1915, 281.)

AN adsorbent is most efficient when the solvent is an acid possessing the same anion, probably owing to diminished solubility of the adsorbent. Nitric acid increases the effect of oxide adsorbents in the same way as sulphuric acid increases that of sulphates, hydrochloric acid that of chlorides, etc. The character of the adsorption is often appreciably altered by small differences in the mode of preparing the adsorbent.—J. R.

*Argon-nitrogen mixtures [for filling half-watt lamps]; Determination of the composition of — by means of liquid air.* L. Hamburger and H. Filippo. *Z. angew. Chem.*, 1915, 28, 75—76.

Two reservoirs, communicating at their lower ends with a mercury levelling tube, terminate above in bent connections, each sealed to one of a pair of German silver tubes, the lower ends of which are closed. One reservoir, with corresponding tube, is permanently filled with pure argon, and the other, after pumping out air, is charged with an equal volume of the gaseous mixture, which is admitted through a coil containing glass wool, at about  $-80^{\circ}\text{C}$ , to remove impurities. The metal tubes are plunged into liquid air, and the difference of mercury level in the reservoirs, that is the difference in vapour pressures, is read off. Each apparatus is calibrated with mixtures of known composition, so that the difference of level gives the percentage of nitrogen present. Results, with an error of about 0.5%, may be obtained in a few minutes.—F. SODN.

#### PATENTS.

*Sulphuric acid from waste pickle [containing iron sulphate]; Recovery of —.* E. Howl, Dudley, and F. Perry, Tipton. *Eng. Pat.* 5830, March 7, 1914.

THE pickle is evaporated until the free acid acquires a concentration of about 75%, whereupon almost the whole of the iron sulphate is precipitated in the anhydrous form.—F. SODN.

*Nitric acid; Process for the production of —.* F. Raschig, Ludwigshafen, Germany. U.S. Pat. 1,130,104, March 2, 1915. Date of appl., April 21, 1914.

NITRIC acid is produced continuously by distilling a mixture of sodium nitrate and sulphuric acid under high vacuum at about  $170^{\circ}\text{C}$ . The fresh mixture is supplied, and the bisulphate removed, through vertical conduits containing heads of liquid corresponding to the vacuum employed.—F. SP.

*Ammonia; Production of liquid anhydrous —.* H. Pollard, Manchester. *Eng. Pat.* 6274, March 12, 1914. Under Int. Conv., Oct. 21, 1913.

PURIFIED ammonia gas is passed into cooled vessels containing crystals of ammonium nitrate. The

salt absorbs one-third of its weight of ammonia, forming a liquid which is completely decomposed at  $190^{\circ}\text{F}$ . ( $88^{\circ}\text{C}$ ), sufficient pressure being developed to liquefy the cooled gas. Moisture, pyridine, and oil are eliminated by the above process. The heat necessary is small as compared with that required to run a compressor.

—W. H. H. N.

*Nitrate of ammonia; Process of making granular* —. F. L. Gallup, Media, Pa., Assignor to E. I. du Pont de Nemours Powder Co., Wilmington, Del. U.S. Pat. 1,131,361, March 9, 1915. Date of appl., May 18, 1912. Renewed July 28, 1914.

AMMONIUM nitrate solution is concentrated to a degree depending on the size of grain required, and the salt is then crystallised by cooling, whilst stirring and aerating the solution.—F. SODN.

*Aluminium nitride; Manufacture of —.* Soc. Générale des Nitrures, Paris. *Eng. Pat.* 24,533, Dec. 24, 1914. Under Int. Conv., Dec. 24, 1913.

A FINELY divided mixture of an aluminous compound and carbon is passed into a flame produced by the combustion of coal dust, the proportion of air for combustion being adjusted to give almost exclusively carbon monoxide. For example, 30 kilos. of bauxite and 12 kilos. of carbon are employed with 100 kilos. of coal dust and not more than 440 cub. metres of air. A heavy-oil or gas blowpipe, or other in-blown flame, may be used to assist the combustion of the coal dust.—F. SODN.

*Double nitride composition of matter. [Fixation of atmospheric nitrogen.]* S. Peacock, Chicago, Ill., Assignor to Internat. Agricultural Corporation, New York. U.S. Pat. 1,123,585, Jan. 5, 1915. Date of appl., May 31, 1913.

A DOUBLE nitride of a metal and a non-metal (especially of calcium and silicon), such as may be produced, together with carbon monoxide, by heating a mixture of carbon, metallic oxide, and silica, to  $1600$ — $2000^{\circ}\text{C}$ , in an atmosphere of nitrogen. Sufficient carbon is used to reduce the silica and form  $\text{SiC}$ , as an intermediate product.—F. SODN.

*Sodium sulphide; Process of making* —. H. K. Moore, Berlin, N.H. U.S. Pat. 1,130,317, March 2, 1915. Date of appl., Aug. 14, 1913.

SODIUM sulphate, sodium carbonate, and a reducing agent, such as carbon, are fed into a heating chamber in which they are melted together and from which the fused reduction product is continuously withdrawn; sublimed material is recovered by passing through a liquid spray.—F. SODN.

*Sulphur and alkali compounds; Process for making and preserving —.* C. E. Hite, Burlington, N.J., Assignor to W. Pincus, Philadelphia, Pa. U.S. Pat. 1,132,476, Mar. 16, 1915. Date of appl., Sept. 19, 1914.

EQUAL quantities of sulphur and soda are heated together at a regulated temperature till the product is substantially soluble in water. The reaction is then arrested and the product sealed to exclude moisture and air, which decompose it to a compound soluble with difficulty in water.—W. H. H. N.

*Silicic acid; Manufacture of soluble, chemically pure* —. Ges. f. Elektro-osmose m. b. H. Fr. Pat. 471,678, April 10, 1914. Under Int. Conv., April 14, 1913.

A SOLUTION of alkali silicate is electrolysed in the anode compartment of a diaphragm cell, fitted



preferably with perforated electrodes applied against the diaphragm wall. The alkali diffuses through the diaphragm into the cathode compartment, which contains water, and by maintaining suitable conditions, *e.g.*, by using a diaphragm of carborundum and corundum, especially of the kind described in Fr. Pat. 426,072 (this J., 1911, 942), the silicic acid remains entirely in the anode compartment. Acid impurities are removed from the silicic acid by similar treatment in the cathode compartment of a diaphragm cell.—F. SODN.

*Rock salt or sea salt; Process for obtaining pure white—by fusion.* F. Strumberg. Fr. Pat. 472,203, May 14, 1914.

SALT is fused by direct or indirect electric heating and agitated by direct passage of an electric current, and the product, after settling, is run into moulds. Sodium phosphate or phosphite or an analogous compound may be added to the fused salt.—F. SODN.

*Boroformates; Manufacture of—.* H. Weitz Auslandes. m. b. H. Fr. Pat. 472,233, May 15, 1914.

AN alkali or alkaline-earth hydroxide or carbonate is dissolved in water in the presence of boric and formic acids or their soluble alkali or alkaline-earth salts. For example, 431 grms. of crystallised sodium carbonate and 575 grms. of borax are dissolved by warming in 1250 c.c. of water, and 347 grms. of 80% formic acid is added; crystals of the composition,  $\text{CBO}_2\text{H}_2\text{Na}_2\text{H}_2\text{O}$ , are deposited on cooling.—F. SODN.

*Graphite; Recovery of— from pieces of used graphite crucibles.* A. Teichmann. Ger. Pat. 279,006, Feb. 7, 1914. Addition to Ger. Pat. 263,653.

THE pieces of graphite are soaked in water instead of being treated with acid as described in the chief patent (this J., 1913, 1068), the subsequent treatment being the same.—A. S.

*Hydrated aluminosilicates or artificial zeolites; Process for the production of—.* R. Gans, Pankow, Assignor to J. D. Riedel A.-G., Berlin. U.S. Pat. 1,131,503, March 9, 1915. Date of appl., Aug. 4, 1911.

SEE Fr. Pat. 425,343 of 1911; this J., 1911, 1014.

*Silicic acid; Manufacture of chemically pure, soluble—.* B. Schwerin, Assignor to Elektro-Osmose A.-G. (Graf Schwerin Ges.), Frankfurt, Germany. U.S. Pat. 1,132,394, March 16, 1915. Date of appl., April 18, 1914.

SEE Fr. Pat. 471,678 of 1914; preceding.

*Washing and bleaching of wool, and recovery of grease and potassium salts.* Fr. Pat. 471,654. See V.

*Absorbent for carbon dioxide in breathing apparatus, etc.* Eng. Pat. 22,719. See XIXB.

## VIII.—GLASS; CERAMICS.

*Glass Research Committee of the Institute of Chemistry; Report of the—.*

THE Glass Research Committee was appointed in October last to conduct investigations with a view to arriving at suitable formulas to be freely available to manufacturers willing to assist in maintaining the continued supply of laboratory glassware. The Committee consisted of Prof. R.

Meldola (then President of the Institute), Mr. B. Blount, Mr. O. Mehner, Prof. H. Jackson, Mr. W. C. Hancock, and Mr. T. R. Merton.

The chief aims of the research have been: (i.) to produce working formulas for all glasses used in laboratory work, and (ii.) to ascertain the influence of various ingredients on the physical and chemical properties of glasses. The work was extended to include glass for miners' lamp glasses, at the suggestion of the Home Office; and also glass for ampoules, to meet the needs of wholesale pharmaceutical chemists engaged in the production of Army Medical requirements. The Committee have also examined and reported on samples of British and French laboratory glassware, produced since the beginning of the war, a number of the specimens being made from formulas similar to, and in some cases almost identical with, those recommended by the Committee. Mixtures prepared in accordance with the analytical results were not always satisfactory; but the analyses were helpful in suggesting synthetic experiments.

Up to the present time, the Research Committee have reported eleven formulas for glasses for various purposes based on the results of about 400 experimental melts on a scale large enough for drawing rods and blowing small vessels. No formula has been issued without submitting the specimens made to rigorous tests to prove their suitability for the purposes for which they are intended. The question of workable temperatures has been carefully considered and, so far as it is possible to judge, the melts on a small scale indicate that even better results will be obtained on the industrial scale. This view has been justified by the samples already received from manufacturers who have tried some of the formulas.

Special attention has been paid to the proportions of basic and acidic substances in respect of the action of glass mixtures on clay crucibles during fusion, and it has been shown by careful investigation that the formulas proposed give melts in which the influence of the ingredients of the crucibles is very slight and in some cases practically inappreciable.

The following formulas have been communicated to a number of manufacturers who have expressed their interest in the progress of the investigation and to scientific workers who are conducting similar experiments.

*Soft Glasses,* suitable for ordinary chemical laboratory ware:—

(1) Sand, 67.0 parts; sodium carbonate ( $\text{Na}_2\text{CO}_3$ ), 34.2; calcium carbonate, 11.6; alumina ( $\text{Al}_2\text{O}_3$ ), 6.5. A soft glass which does not give up alkali readily to water, works well in the blowpipe and does not devitrify readily.

(2) Sand, 67.0 parts; sodium carbonate, 29.0; calcium carbonate, 9.6; calcium fluoride, 1.6; alumina, 8.3; boric anhydride ( $\text{B}_2\text{O}_3$ ), 2.0. A soft glass of higher quality. Does not give up alkali under severe tests. A kindly working glass before the blowpipe, and very difficult to devitrify.

*A Resistant Glass* suitable for pharmaceutical purposes, ampoules, etc.:—

(3) Sand, 67.0 parts; alumina, 10.0; calcium carbonate, 12.5; magnesia, 0.5; potassium nitrate, 1.0; sodium carbonate, 17.0; boric anhydride, 8.0. This glass is intermediate in hardness between soft glass and combustion tubing, is highly resistant to chemical action, withstands changes of temperature well, and should be a very suitable glass for high class beakers, flasks, etc.

*Glasses for Combustion Tubing:*—

(4) Sand, 68.2 parts; alumina, 6.2; barium carbonate, 8.8; calcium carbonate, 13.0; potassium nitrate, 4.3; sodium carbonate, 5.5; boric anhydride, 5.5; calcium fluoride, 1.0. This glass resembles Jena combustion tubing very closely indeed. It has practically the same fusing point.

It fuses on to Jena glass perfectly, and is indistinguishable from it before the blowpipe and in its behaviour on prolonged heating below its fusing point. The presence of the small quantity of calcium fluoride facilitates the incorporation of the ingredients. The sodium carbonate can be reduced to 1.84 parts provided 7.93 parts of anhydrous borax be used in the place of boric anhydride.

(5) Sand, 68.2 parts; alumina 6.2; barium carbonate, 8.8; calcium carbonate, 14.2; potassium nitrate, 4.3; sodium carbonate, 5.5; boric anhydride, 5.5. This glass is practically of the same composition as (4). It is not so easy to make or to work, but it does not become so opaque as Jena combustion tubing on prolonged heating. As in No. (4), the proportions given for sodium carbonate and anhydrous borax can be substituted for the figures for sodium carbonate and boric anhydride.

*Miners' Lamp Glasses:—*

(6) Sand, 65.0 parts; alumina, 1.0; calcium carbonate, 0.6; arsenious oxide, 2.0; antimony oxide, 1.0; potassium nitrate, 3.0; sodium carbonate, 14.0; boric anhydride, 21.0. A colourless and fusible glass withstanding rapid changes of temperature exceptionally well.

(7) Sand, 65.0 parts; alumina, 1.0; calcium carbonate, 0.6; arsenious oxide, 2.0; antimony oxide, 1.0; potassium nitrate, 3.0; anhydrous borax, 20.68; boric anhydride, 5.5. The same glass as (6) but the ingredients have been varied to avoid the use of so much boric anhydride, which is at present apparently difficult to obtain on a commercial scale.

*Resistance glass:—*

(8) Sand, 65.5 parts; alumina, 2.5; magnesia, 5.0; zinc oxide, 8.0; sodium carbonate, 19.2; anhydrous borax, 13.0. A glass almost identical in its general behaviour with Jena resistance glass; withstands changes of temperature well, but, like Jena, is not suitable for working before the blowpipe. It darkens and tends to devitrify; operations—such, for instance, as sealing side tubes into flasks—are difficult, if permanent and neat joints are required.

Formula No. 3, recommended for pharmaceutical purposes, ampoules, etc., may be substituted for the resistance glass with advantage, as the ampoule glass lends itself very well to blowpipe work, and is also especially resistant chemically.

*Alternative for combustion tubing:—*

(9) Sand, 72.0 parts; alumina 10.0; calcium carbonate, 11.0; magnesia, 0.5; potassium nitrate, 3.0; sodium carbonate, 11.2; borax anhydrous, 7.2. This glass is capable of withstanding high temperatures and rapid changes of temperature; works well before the blowpipe and is free from the chief defect of Jena glass, namely, the readiness with which it becomes cloudy and finally quite opaque after prolonged use.

By slight modifications of this formula, almost any degree of hardness can be obtained.

In formulas (8) and (9) substances such as magnesia and zinc oxide can be added in the form of carbonates if the actual percentages of MgO and ZnO respectively present in the carbonates are known.

*Soft Soda-Glasses suitable for tubing and for X-ray bulbs:—*

(10) Sand, 68.0; alumina, 4.0; calcium carbonate, 12.8; potassium nitrate, 14.5; sodium carbonate, 26.0; and

(11) Sand, 68.0; alumina, 4.0; calcium carbonate, 12.8; potassium carbonate, 10.0; sodium carbonate, 26.0. These glasses do not lose their easy-working qualities after repeated heating and blowing, and are plastic over a long range of temperature. They require a temperature of at least 1400° to 1500° C. for complete incorporation

of the ingredients in order to obtain that homogeneity which is necessary for resistance to rapid changes of temperature and ease of working before the blowpipe. No. (10), containing potassium nitrate, is considered the better of the two, and is more easily incorporated.

The Committee is of the opinion that there is now information available for the manufacture of all the important glasses used in the laboratory and for industrial purposes, which have hitherto been mainly obtained from abroad.

*Glass for optical instruments. Report of the British Science Guild. Chem. News, 1915, 111, 178—180.*

In a report presented to the Government by the British Science Guild, on the manufacture of optical instruments in this country, it is stated that the Guild is satisfied that the supply of optical glass for telescopes, binoculars, range-finders, and other service instruments, is sufficient for the purpose. As regards glass for photographic and microscopic lenses, a greater variety of glasses should be available than are at present manufactured in this country. The attention of the authorities might be drawn to the opportunity for developing British glass manufacture in this direction. The defective supply of pure barium compounds is understood to be a difficulty. Barium glass of high refraction and low dispersion is reported to be especially difficult to obtain. Attention is also called to the desirability of the provision of facilities for research, and to the necessity for finding a refractory lining of the melting pot which would resist the action of the materials used at the working temperature. The Guild therefore recommends:—(a) That better provision should be made at the National Physical Laboratory for the testing of samples of glass as to their physical and optical properties. (b) That facilities should be provided as speedily as possible for the carrying out, at the National Physical Laboratory, or elsewhere, of the researches connected with the manufacture of optical glass referred to in this report. (c) That steps should be taken as speedily as possible to provide facilities for systematic, scientific, and manual training in technical optics.

*Optical qualities of glass plates; Sensitive method for examining some ——. Earl of Berkeley, and D. E. Thomas. Phil. Mag., 1915, 29, 613—617.*

THE Zeiss interferometer may be used for examining the optical qualities of glass plates—echelon spectroscopy plates, etc.—by measuring the difference in the displacement of the interference bands when light (the green mercury line is suitable) traverses the plate placed first at 45° to the optic axis in front of the silvered reflecting mirror, and then when rotated through 180°. The factor measured is  $D(\mu-1)$  and it is the constancy of this product which is the essential condition for a perfect echelon plate, and not  $D\mu$ , the factor determined by Michelson's method, which method also is some 30% less sensitive.—G. F. M.

PATENTS.

*Glass; Composition for making ——. O. Schott, Assignor to Schott and Gen., Jena, Germany. U.S. Pat. 1,130,767, March 9, 1915. Date of appl., Sept. 12, 1912.*

The glass contains at least 50% of silicic acid, and has as its other glass-forming components, alumina 4 to 15 (6 to 12)%, lime 3 to 11%, boric acid 5 to 15%, and soda 8 to 12%, the total percentage of alumina and lime being at least half, and at most five times that of the boric acid.—W. C. H.

*Ceramic materials; Process of shaping* —. E. R. Berry, Malden, Mass., Assignor to General Electric Co., New York. U.S. Pat. 1,131,463, March 9, 1915. Date of appl., June 21, 1913.

A MIXTURE, for example, of clay, talc, and sodium silicate in the moist state, is extruded under pressure, and the articles formed are air-dried, baked at about 130° C., machined, and finally hardened by firing to about 800° C.—W. C. H.

*Clay and like materials; Process of treating [removing iron from]* —. F. Thompson, Newark, Del., Assignor to The Crescent Clay Refining Co., Baltimore, Md. U.S. Pat. 1,132,537, March 16, 1915. Date of appl., Aug. 23, 1913.

CLAY is treated with dilute hydrochloric acid under heat and steam pressure, whereby the iron compounds are removed in solution without decreasing the plasticity of the clay. The acid may be added direct or formed *in situ* by the action of another acid on an alkali chloride.—A. B. S.

*Binding medium for granular materials; Production of a "non-greasy" — from "fat" clay.* M. Bertram. Ger. Pat. 279,385, May 11, 1911.

A SLOP made from "fat" clay is mixed with Portland cement or other materials (slag cement, iron Portland cement) containing decomposable calcium silicates, and allowed to stand. By this treatment the clay is converted into a non-plastic product suitable as a binding medium for granular materials, and which, unlike "fat" clay, can be treated satisfactorily in a filter-press.—A. S.

## IX.—BUILDING MATERIALS.

*Cement drain tile; Investigation of the durability of — in alkali soils.* R. J. Wig. G. M. Williams, and others. U.S. Bureau of Standards. J. Franklin Inst., 1915, 179, 354—356.

A PRELIMINARY report on the behaviour of over 8000 cement drain tiles after 12 months' practical use in various American States, where they were exposed to the action of alkali water, fresh water, and ordinary weathering. The tiles were manufactured from 16 different mixtures varying from the leanest to the richest commercially practicable. Those containing not less than 1 part of cement to 3 of aggregate were apparently unaffected structurally in the very concentrated alkali soils of Grand Junction and Montrose, Colo., and Garland, Wyo.; and those consisting of 1 part of cement to 4 of aggregate (the leanest mixture employed) were similarly unaffected by the concentrated alkali soils of Fort Shaw, Mont., Sunnyside, Wash., Yuma, Ariz., and Roswell, N.M.—W. E. F. P.

*Heat-conductivity of refractory building materials; Determination of the —.* E. Heyn. Stahl u. Eisen, 1914, 34, 832—834. Z. angew. Chem., 1914, 27, Ref., 722.

THE following method is used in the Kgl. Materialprüfungsamt, Gross-Lichterfelde West. The block of material to be tested is built into a structure of blocks of the same or a similar kind, and is in contact at one end with a slab of highly refractory material which is heated electrically by means of a granular carbon resistance. At regular intervals of time, the temperatures at different parts of the block along its longitudinal axis are observed by means of thermo-elements, and curves are plotted with the times as abscissae and temperatures (difference between the atmospheric and observed temperatures) as ordinates.—A. S.

*Timber preservatives; Risk of poisoning by* —. F. Moll. Z. angew. Chem., 1915, 28, 73—75.

THE relative activities of various preservatives and their virulence as poisons (measured as reciprocals of lethal doses) are tabulated and shown to exhibit, as a rule, about the same ratio.—F. SODN.

*Mercuric chloride; Risk of poisoning by volatilised* —. F. Moll. Z. angew. Chem., 1914, 27, 559. Chem.-Zeit., 1915, 39, Rep. 59.

THE fatal dose of 0.2 grm. of mercuric chloride is contained in 500 cb. metres of air completely saturated with the vapour at 20° C. Since this volume of air suffices a human being for 50 days, any danger of poisoning by the occasional inhalation of air contaminated with volatilised mercuric chloride, e.g., from wood impregnated with that substance, may be dismissed.—J. R.

*Jungner's method of polish extraction from feldspar, etc., in cement burning.* See VII.

## PATENTS.

*Cement; Manufacture of* —. J. F. Goddard, London. Eng. Pat. 13,542, June 3, 1914.

A MIXTURE of 1 part of tannin and 5 parts of gypsum with sufficient water to make a paste is allowed to dry and is then ground to powder. This powder is mixed with Portland cement clinker, which is then ground in the usual manner, the temperature not being allowed to exceed 300° F. The addition of tannin makes the cement stronger and more waterproof and does not affect its soundness.—A. B. S.

*Rotary [cement] kilns; Lining for* —. Dynamidon G. m. b. H. Fr. Pat. 472,033, May 11, 1914. Under Int. Conv., July 31, 1913.

WHEN a layer of non-conducting material is interposed between the outer casing and the refractory lining of a rotary kiln to reduce the loss of heat by radiation, the lining is rapidly attacked by the clinker when made of ordinary refractory bricks. This difficulty is overcome by using a special brick containing over 60% of fused alumina for the lining.—W. H. C.

*Concrete; Process of treating masses of* —. C. Ellis, Montclair, N.J., Assignor to New Jersey Testing Laboratories. U.S. Pat. 1,130,717, March 9, 1915. Date of appl., Sept. 25, 1911.

THE surface of concrete masses is roughened by the removal of very fine cement material, impregnated with a water-resistant binding material, and the depressions of the surface are filled to the level of the peaks with a dust-preventing, waterproof, organic binding material. By this means the wear is taken substantially by the peaks of aggregate or sand in the concrete.—W. C. H.

*Acid-proof and fireproof material; Manufacture of an* —. I. Schlossberg. Ger. Pat. 279,386, May 24, 1913. Addition to Ger. Pat. 258,683.

THE material prepared as described in the chief patent (this J., 1913, 605), although capable of withstanding very high temperatures, is deficient in strength between 800° and 1200° C. To overcome this defect powdered glass or powdered brick is incorporated, so that sintering takes place at the temperature range in question. Quartzite is mixed intimately with colloidal silicic acid and calcium oxide or hydroxide, powdered brick is added, and the mass is formed into blocks which are hardened in the usual way.—A. S.

*Cement; Process for manufacturing a hydraulic*  
— A. V. Carlson, Degerhamn, Assignor to  
C. L. Carlson, Stockholm, Sweden. U.S. Pat.  
1,130,143, March 2, 1915. Date of appl., Feb. 8,  
1913.  
SEE Fr. Pat. 452,399 of 1912; this J., 1913, 659.

*Production of tar oils which may be used as paint  
oils and with increased antiseptic and fungicidal  
properties.* Fr. Pat. 471,071. See III.

### X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.

*Iron, cobalt, and carbon; The chemical and mechani-  
cal relations of—* J. O. Arnold and A. A.  
Read. Inst. Mech. Eng., Mar., 1915. Engineer-  
ing, 1915, 99, 362—364.

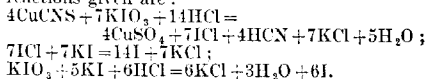
AN investigation of 5 steels containing C 0.62—0.93,  
Co 2.68—20.85, Si 0.05—0.11, Mn 0.16—0.25, P  
and Al each less than 0.02, and S less than 0.04%.  
The forged specimens were all "tough" in the  
lathe but easily machinable, the tenacity being  
gradually increased, and ductility and resistance to  
alternating stress decreased, by increasing  
cobalt. The carbides—separated from the speci-  
mens by electrolysis in dilute hydrochloric acid  
(sp. gr. 1.02) with a current density of 0.18 amp.—  
varied in composition between 50Fe<sub>3</sub>C+Co<sub>3</sub>C and  
8Fe<sub>3</sub>C+Co<sub>3</sub>C, and contained only 5—6% of the  
total cobalt present in the steels. By annealing  
steels containing 2.68, 5.5, and 11.18—20.85% Co,  
15, 74, and 100%, respectively, of the combined  
carbon was converted into graphite. Cobalt is  
less effective than nickel in precipitating graphite,  
and forms no definite solid solution corresponding  
to Fe<sub>3</sub>Ni.—W. E. F. P.

*Steel at moderately high temperatures; Elastic pro-  
perties of—* F. E. Rowett. Proc. Roy.  
Soc., 1915, A, 91, 291—303.

UNDER alternating torsional stress applied at  
5 secs. per cycle, hard-drawn, unannealed steel tube

*Copper in steel; Determination of—* W. D.  
Brown. J. Ind. Eng. Chem., 1915, 7, 213.

FIVE grms. of the steel is dissolved in a mixture of  
40 c.c. of nitric acid of sp. gr. 1.20 and 25 c.c. of  
sulphuric acid (1:1), the solution is evaporated  
to expel nitric acid, cooled, and diluted to 400 c.c.  
with hot water. When the ferric sulphate is  
completely dissolved, 50 c.c. of strong ammonium  
bisulphite solution is added, with stirring, and  
then 25 c.c. of a 5% solution of potassium thio-  
cyanate: precipitation of the copper is complete  
after boiling for 5 mins., and the cuprous thio-  
cyanate is filtered off and washed with cold 1%  
sulphuric acid solution. The paper with the  
precipitate is then treated with 20 c.c. of hydro-  
chloric acid (1:1) and a quantity of standard  
potassium iodate solution (19.61 grms. KIO<sub>3</sub> per  
litre; 1 c.c.=0.005 gm. Cu) corresponding to  
2 c.c. for each 0.1% Cu expected. The mixture  
is diluted to 500 c.c., treated with a volume of a  
10% solution of potassium iodide equal to that  
of the iodate solution added previously, and the  
free iodine titrated with thiosulphate of strength  
equivalent to that of the iodate solution: the  
difference between the volumes of the iodate and  
the thiosulphate corresponds to the copper. The  
reactions given are:



—A. S.

*Blister copper; Occurrence of some of the rarer  
metals in—* A. Eilers. Trans. Amer. Inst.  
Min. Eng., 1914, 47, 217—218.

THE relative proportions of metals recovered from  
100 tons of blister copper at 8 refineries are given  
below. Ores treated at No. 1 and 2 occur in  
porphyry. No. 3 treats concentrated copper-lead  
mattes from different lead smelters of the Rocky  
Mountain region. Nos. 4 and 5: ores occur near  
diorite. No. 6 works up mattes resulting from the  
smelting of silver and gold ores with low-grade  
copper ores, from all parts of Mexico. At No. 7, the  
ore comes from veins found in limestone near  
andesite.

No.	Refinery	Au	Ag	Pt	Pd	Se	Te	Bi	Ni
		oz.	oz.	oz.	oz.	lb.	lb.	lb.	lb.
1	Garfield, Utah	288	3486	0.342	1.183	36.0	5.54	6.1	40
2	Steptoe, Nev.	169	550	1.016	4.402	110.1	none	0.33	64
3	Omaha, Nebr.	360	23,000	1.825	6.486	26.6	67.1	18.6	944
4	Mountain, Cal.	1418	10,960	1.329	0.007	36.0	3.3	27.3	11.5
5	Tacoma, Wash.	2187	8710	0.710	3.327	42.0	none	5.7	770
6	Agua Calientes	489	67,300	0.416	0.226	170.0	none	4.0	12
7	Cerro de Pasco	170	9900	0.319	0.589	13.7	none	13.5	32
8	Mount Lyell	464.5	7205	0.624	1.374	42.0	none	4.3	166

—W. R. S.

was only slightly less elastic at about 300° C. than  
at ordinary temperature, but flowed perceptibly  
when the stress was applied at 15 mins. per cycle,  
the area of the closed stress-strain loop in the latter  
case being about 4 times that in the former; with  
annealed tube at 300° C., the energy lost per cycle  
was almost independent of the time. At about  
540° C., hard-drawn tube flowed rapidly, and for  
a long period, under a shear stress of less than  
1 ton per sq. in., and when the stress was suddenly  
removed, the immediate elastic recovery was  
followed by a slow, backward flow which persisted  
for several minutes; under the same conditions,  
annealed tube also exhibited some flow and elastic  
after-working, but both were much less than in the  
hard-drawn tube.—W. E. F. P

*Copper ores; The smelting of—in the electric  
furnace.* D. A. Lyon and R. M. Kenney. Trans.  
Amer. Inst. Min. Eng., 1914, 47, 233—270.

THE electric furnace is intended, not to replace the  
reverberatory or blast-furnace in the smelting of  
copper ores, but to be used as a substitute for them  
in localities where fuel is dear but hydro-electric  
power easily available. The reverberatory, as  
well as the blast furnace in ordinary coke smelting,  
is essentially a means of melting the charge, and  
this can be done in the electric furnace with a much  
higher heat efficiency. Michigan native-copper  
concentrate (Cu 37.35%) smelted in a Siemens  
electric furnace gave black copper assaying 98.59%,  
with a slag loss of 0.15%. The volatilisation loss  
was smallest when producing a low-melting,

monosilicate slag. Power and electrode consumption are given as less than 640 kilowatt-hours per ton of ore and 10 lb. per ton of charge, respectively. Matte-smelting experiments were made with low-grade pyritic, silicious, and roasted ores; the slag and volatilisation losses were low, and power and electrode consumption are given as 480 kilowatt-hours per ton of ore, and 5 lb. per ton of charge. A discussion on the adaptability of the electric furnace to partial pyritic and pyritic smelting is added.—W. R. S.

*Copper-zinc alloys: Hardness of* —. D. Meneghini. *Annali Chim. Appl.*, 1915, 3, 95—101.

THE hardness was determined by a ball test, using a steel ball of 2.9 mm. diameter and a load of 10.87—25.15 kilos., and measuring the indentation under the microscope with the aid of a micrometer. The results confirm Guertler's generalisation that a diminution in electrical conductivity is accompanied by an increase in hardness.—A. S.

*Zinc: Determination of* — in ores and pyrites cinder. H. Rubricius. *Chem.-Zeit.*, 1915, 39, 198.

THE method is specially applicable to materials containing zinc in small quantities. Five grms. of the finely powdered substance is heated to boiling with 15 c.c. of concentrated hydrochloric acid, and after about 15 mins. a few c.c. of strong nitric acid is added, and the whole concentrated to a very small volume. If it solidifies on cooling it should be gently warmed again with a few drops of hydrochloric acid. The cold residue is mixed with 30 c.c. of concentrated ammonia and filtered, the treatment with ammonia is repeated two or three times, and finally the filter is washed with hot water. If the liquid is not distinctly blue a few drops of dilute copper sulphate solution are added, as the presence of copper sulphide facilitates the subsequent filtration of the zinc sulphide. The liquid is heated to boiling and treated with a few crystals of sodium sulphide. After a short time the precipitate is filtered off, washed with hot water, and at once extracted with hot hydrochloric acid which dissolves the zinc (oxidation of the copper sulphide must be avoided). The acid solution of zinc is precipitated by sodium carbonate and the zinc weighed as oxide. If manganese is present it may be removed from the mixed sulphide precipitate by dilute acetic acid, or it may be precipitated from the ammoniacal liquid by means of ammonium persulphate or bromine.—J. H. L.

*[Tin] dross [and zinc slags]: The smelting of* —. in the electric furnace. R. S. Wile. *Amer. Electrochem. Soc. Min. and Eng. World*, 1915, 42, 501—504.

AT the works of the American Sheet and Tin Plate Co., Demmler, tin dross is smelted in shaft furnaces of greater depth than diameter, employing direct current at 220 volts and 800—1000 amp. After the initial formation, by arcing, of a molten slag containing  $\text{SiO}_2$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$  in the proportions of 4:1:1, respectively, the furnace is worked on the resistance principle, a mixture of the dross with carbon and sufficient silica to maintain the silica content of the slag being charged continuously. The temperature of the slag is kept above 3000° F. (1650° C.) to reduce the dross rapidly and to prevent the formation of tin silicates; the tin content of the slag under these conditions is about 0.5%. The power is about 350 kw. per ton for dross containing 30, Zn 8—12, and Fe 10—18%, the temperature of the furnace being 93—95. A type has been successfully employed for the smelting of molten zinc slags by a process

depending on the formation of easily fusible zinc-ferro-silicates and the subsequent decomposition of these (with volatilisation of the contained zinc oxide) by lime at a high temperature.

—W. E. F. P.

*Tin, antimony, and arsenic: Rapid analysis of alloys [matte, slags, etc.] for* —. F. A. Stiel. *J. Ind. Eng. Chem.*, 1915, 7, 211—212.

THE following methods have been used for six years with satisfactory results:—*Alloys*. 0.5 gm. of fine shavings or drillings is dissolved in 8 c.c. of concentrated sulphuric acid, the solution is boiled, cooled, treated with 5 c.c. of cold water, cooled, and 20 c.c. of concentrated hydrochloric acid and about 0.5 c.c. of granulated pumice are added. The solution is then distilled gently for 12—15 mins., the temperature being kept at 107° C. (bulb of thermometer 1 in. above surface of liquid) for at least 5 mins.; the exit tube for the vapours is bent downwards and connected with an S-tube, one bend of which is nearly filled with water and submerged in cold water, whilst the free end dips into about 75 c.c. of water in a beaker. The distillate, amounting to about 200 c.c., is treated with an excess of about 2 grms. of sodium bicarbonate, warmed to 27° C., and the arsenic determined by titration with iodine solution (1 c.c. = 0.010672 gm. I or 0.00315 gm. As), in presence of starch, to a blue tint corresponding to that obtained with 0.2 c.c. of iodine solution in a control determination. The residue in the distilling flask is diluted with about 130 c.c. of water and titrated with permanganate solution (2.6315 grms. per litre; 1 c.c. = 0.005 gm. Sb). The solution is then, if necessary, mixed with sufficient antimony trichloride to bring the antimony content up to 0.07 gm., 6 c.c. of concentrated sulphuric acid, 60 c.c. of concentrated hydrochloric acid, and about 6 ins. of clean, soft No. 14 pure iron wire are added, the solution is boiled gently for ½ hour, and after adding 4—6 ins. more of iron wire, again boiled for ½ hour. A rubber stopper is placed loosely in the neck of the flask, and, after two minutes, the flask is stoppered tightly, cooled in water, the solution transferred to a beaker, the flask rinsed with 150 c.c. of recently boiled water, and the solution (300—350 c.c.) titrated with the iodine solution (see above; 1 c.c. = 0.005 gm. Sn) to a blue colour corresponding to that given by 0.4 c.c. of the iodine solution. When more than 3% Cu is present 0.5—1 gm. of potassium iodide crystals is added just before titrating the tin.

*Matte, soluble furnace products, chilled slags, etc.* Antimony and tin may be determined directly and rapidly by the following method, even when much copper, iron, and arsenic are present: 0.5 gm. of the sample is heated for at least 15 mins. with 10 c.c. of concentrated sulphuric acid; if much silicon is present 15 c.c. of water is added before the acid. The cooled solution is treated with 10 c.c. of water and 10 c.c. of hydrochloric acid, boiled for 2 mins., treated with at least 1.5 grms. of potassium chlorate, heated to expel chlorine and chlorine compounds, treated with about 0.1 gm. of sulphur, and boiled for ½ hour. After cooling, the solution is diluted with 6 c.c. of water, cooled, treated with 20 c.c. of concentrated hydrochloric acid and some pumice, boiled to expel arsenic, and antimony and tin determined as described above. If much carbon is present, nitric acid is used in place of potassium chlorate, and somewhat more sulphur is added subsequently. Slags or ores containing insoluble stannic oxide or silicate must first be fused with caustic soda.—A. S.

*Tungsten: Occurrence and output of* —. *Engineering*, 1915, 99, 442—443.

TUNGSTEN is widely distributed throughout the earth's crust, there being few countries in which

it has not been found. The following figures give the production, in tons of 60%  $WO_3$  concentrates, as far as it is known:—

	1912.	1911.	1910.	1909.	1908.	1905.
<b>Europe:—</b>						
Portugal.....	982	1140	1320	609	684	320
England.....	193	266	274	376	233	172
All other countries	623	610	584	430	597	750
<b>America:—</b>						
United States...	1207	1120	1821	1619	671	303
Argentina.....	637	800	1061	990	548	—
Peru.....	—	500	100	—	—	—
All other countries	243	265	315	168	187	75
<b>Asia and Africa:—</b>						
India.....	1698	400	396	7	—	—
Elsewhere.....	175	183	169	153	—	—
<b>Australasia:—</b>						
Queensland.....	928	900	1145	670	516	1582
New Zealand.....	—	190	187	78	87	64
Elsewhere.....	67	310	325	291	182	240

**Portugal.**—The Borralha mines in the Castello Branco district are the chief producers; the concentrates contain 70 to 72%  $WO_3$ , and are free from tin, sulphur, bismuth, or phosphorus. The tungsten is found in quartz veins, and in some localities it is also disseminated through granites. The Portuguese output is exported to Great Britain, France, and Germany. Within the last two years tungsten mines have been opened out on concessions in the Concelho of Sabrosa and Villareal, the total area exceeding 3000 hectares. The average content when the mines were started was found to be 70%  $WO_3$ , and even reached 75%, although the concentrating methods were imperfect. Most of the labour of picking, crushing, and concentrating is cheap local handwork, until improved methods can be made available. Water power from the River Pinhao is available for electric-power installation.

**Great Britain, Spain, and France.**—Wolframite occurs in the tin ores of Cornwall, from which it has to be separated and recovered; the output during recent years has found a ready market in Germany. In Spain the ore is found in the Marmolejo district of Andalusia; improved milling facilities and increased mining developments are noteworthy during the last four or five years. In France the ore occurs in the St. Leonard district, Haute Vienne, and in the Limousine district.

**The United States.**—The United States output in 1910 reached 1821 tons of 60% tungsten trioxide concentrates. The Boulder County field in Colorado, and the Atolia field in California, have for many years been the largest producers in the States. When the steel market is overstocked, the larger mines close down. The Colorado ore is a ferberite (iron tungstate) with rather less than 60%  $WO_3$ ; whilst the Californian ore is scheelite, averaging 67%  $WO_3$ ; the veins vary from stringers to a width of 4 ft. There are mines of lesser importance in Arizona, both scheelite and wolframite; in Nevada, tungsten-bismuth ores; in Idaho, ores of hübnerrite and wolframite; also in Washington, where a wolframite is found, which is exported to Germany; some of these mines and mills are owned in Germany.

**Canada.**—Tungsten has been found in many places in Canada, but there is only one mine of any extent, on a deposit in Nova Scotia, consisting of scheelite. It is in the central part of Halifax County, 12 miles from the Atlantic coast. Hübnerrite occurs in Cape Breton island; both wolframite and scheelite are found in the Kootenay district, B.C., but elsewhere the mineral has not been found in commercial quantities.

**Asia.**—Tungsten deposits are mined in India and in Tonkin, and some quantities of wolframite are recovered from the cassiterite in nearly all the important tin-mining centres of Malacca and the East Indies. In India wolframite occurs in schists and granites in the Mergui and Tavoy districts, in Lower Burma. A small quantity has been obtained from the southern Shan States. In Burma wolframite is the main object of exploitation, cassiterite being a sort of by-product, although occasionally the tin ore forms a larger percentage of the alluvial deposits than the wolframite.

**South America.**—Tungsten deposits are very numerous, and have been worked on a profitable scale throughout the central portion of the Cordilleras, including Argentina, Chile, Bolivia, and Peru. The mine with the largest output in the world—the Hauria Sociedad de Minas—is in Argentina; the ore ranges from 65 to 75% concentrates; the bulk of the output in normal times is exported to Germany. The very extensive deposits of low-grade tungsten ore found in Bolivia are only worked when the demand for the metal is good. The largest deposits occur near Izara, in the Province of Inquisivi. The ore is a tungstate of iron and manganese, assaying in the pure form about 75%  $WO_3$ . It occurs in quartz veins in a pyritiferous diorite; about 50%  $WO_3$  is the average of the crude ore. Deposits are also known in Potosi, and in the Cochabamba and Oruro Departments.

In Peru there were important tungsten mines in the province of Angaraco, from which, however, there has not been any very recent output. Considerable development work was reported some time ago on the Conchico, or Huaura deposits in the Pallasca province, Ancacha; these mines are 13,000 ft. to 14,500 ft. above sea-level. The ore is a hübnerrite, occurring in at least two main quartz reefs 15 ft. to 75 ft. in thickness. An ore body of 112,500,000 tons has been reported, of which 10% is estimated as minable, containing 1% of hübnerrite (75%  $WO_3$ ); there is enough 2% ore to provide an output for many years. In Chile thin veins of tungsten associated with bismuth and other minerals are known to exist at Agua Colgada, in the Carrizal district, not far from Huasco.

**Australia.**—There are important deposits of tungsten ore in South Australia in the Tankalella field, not far from Adelaide; also in Queensland and New South Wales. Some of the ore is wolframite, bismuth-wolframite, and scheelite. The Queensland tungsten comes from the Heberton field and the Chillagoe or Hodgkinson river field. The ores are generally in quartz veins, usually accompanied by tin ore near granite contacts, but some veins are free from tin. In New South Wales tungsten and tin occur together, the former as wolframite and scheelite. Tasmania and New Zealand also have tungsten deposits.

The selling value of tungsten is based on a unit of 1%  $WO_3$  per ton. During the first half of 1914, up to the commencement of the war, the value of the unit was 22s. 6d. At the commencement of 1913 it was 23s. 9d.; during the spring of that year it rose to 26s. 8d., and continued at that level all through the year, when it fell to 22s. 6d. During the latter half of 1911, and during the spring of 1912, it was as high as 31s. 3d., but in April of the latter year it fell to 20s. 10d., and it continued at that level until December, when it rose to 23s. 9d.

**Concentration.**—The concentrating-mill of a tungsten-ore mine with electro-magnetic separation may be described as follows:—The ore from the mine is dumped over grizzlies at the shaft-house, the fine going to the bin, whilst the coarse is conveyed to the sorting-table, where it is readily hand-picked, the ore going to the bin, and the waste rock to the dump. From the sorting-room ore-bin the ore is hoisted to the ore-bin in the

mill building, the fines passing through a  $\frac{1}{2}$ -in. grizzly, and the coarse through a crusher set to  $\frac{1}{2}$  in., the whole passing through a shoot and, by bucket elevators, to a main storage-bin of large capacity—100 to 150 tons. The ore is then crushed, wet, by rolls, the product from the rolls going to the trommel, the over-size returning to the rolls, the fines going to three cone sizers and then to two slow-current spitzkastens, distributing to tables and the slime-table. The concentrates from the tables are conveyed to drainage boxes and then to a steel drying-table, from which they pass to a roaster hopper and revolving roaster. An electric magnetic separator follows, from which the tungsten concentrates are bagged. The mill equipment may be operated by engines of 50 horse-power and 30 horse-power, the larger engine being required for the crushing department, and the smaller one for the concentrating section.

*Alloys; Formation of—by electrolysis.* G. Bruni and M. Amadori. Atti R. Accad. Sci. Let., ed. Arti, Padova, 1913—14, 30, 319. Annali Chim. Appl., 1915, 3, 147.

On electrolyzing solutions of mixed salts of two metals (Cu—Ni, Fe—Ni, Fe—Co, Ni—Co) capable of forming solid solutions in all proportions, the deposits contained the two metals in proportions varying with the composition of the solution and with the current density and voltage. With moderately high current density and voltage the ratio between the two metals in the deposit was, in general, approximately the same as in the solution, but with low current density and voltage a larger proportion of the less electropositive metal was deposited. In the case of nickel and iron, using low current density (0.05 ampere per sq. dm.), solutions in which the proportion of iron varied from 40 to 75% yielded deposits in which the iron content was practically constant at 52%. Solutions of iron and cobalt salts in which the proportion of iron varied from 33–50% also yielded deposits of constant iron content. In the case of copper and nickel, and copper and cobalt, the percentage of nickel or cobalt in the deposits was increased by adding ammonia or an ammonium salt and diminished by rotating the cathode.—A. S.

*Alloys; Quantitative effect of rapid cooling upon the constitution of binary—.* Part III. G. H. Gulliver. Inst. of Metals, March, 1915. [Advance proof.] 31 pages.

A CONTINUATION of previous work (J. Inst. Metals, 1913, 9, 120; 1914, 11, 252), leading to the establishment of formulae by which the constitution of an alloy cooled at a rate not consistent with equilibrium can be calculated from the data of the equilibrium diagram. From the calculated results the apparent solidus curve of the alloys for a given rate of cooling can be drawn. For a rate of cooling between extremely slow and extremely fast, the proportion of liquid, or eutectic, in a binary alloy of simple type, at a temperature just above the eutectic or transition point, is given by a formula

of the type:  $\left(\frac{X-x}{X_E-x}\right)^n$ , where X is the percentage

of one component in the alloy,  $X_E$  is the percentage of that component in the liquid or eutectic, and x is the apparent saturation limit of the solid solution at the rate of cooling in question. If the

liquidus and solidus are straight,  $n=1+\frac{X_s-x}{X_E-X_s}$ ,

where  $X_s$  is the percentage of the one component in the saturated solid solution; when the liquidus and solidus are curved, n is a more complex function of X,  $X_E$ ,  $X_s$ , and x. The calculated

results for Pb-Sn and Al-Cu alloys agreed satisfactorily with the experimental results of Degens (this J., 1909, 1041) and of Gwyer (this J., 1908, 1066) respectively. The results calculated for Al-Sn alloys from the equilibrium diagram of Shepherd (this J., 1904, 826), in conjunction with the experimental results of Gwyer (this J., 1906, 639), indicated that the saturation limit of 20% Sn given by Shepherd for the aluminium-rich solution is too high; examination of some annealed alloys showed that the real limit is probably below 10% Sn.—A. S.

#### PATENTS.

*[Iron] ores; Process of reducing—.* A. E. Greene, Chicago, Ill. U.S. Pat. 1,129,862, March 2, 1915. Date of appl., July 15, 1912.

ORES containing phosphorus are partially reduced with a suitable solid reducing agent in an electric furnace in presence of lime, the reduction being completed with a reducing gas not capable of reducing calcium phosphate.—W. R. S.

*Steel; Vacuum process for production of—.* E. Dolensky, Frankfurt, Germany. U.S. Pat. 1,131,488, March 9, 1915. Date of appl., Oct. 22, 1912.

THE molten metal is cleared by subjecting it to the action of a vacuum in a preheated clearing-vessel.—W. R. S.

*[Silicon steel] alloys; Method of making—.* A. Smith, Leetonia, Ohio, Assignor to The Youngstown Iron and Steel Co., Youngstown, Ohio. U.S. Pat. 1,131,799, March 16, 1915. Date of appl., Sept. 18, 1914.

HIGH-SILICON steel is produced by pouring an entire charge of refined steel from an open-hearth or other furnace into a ladle, then withdrawing a fraction, not exceeding 25 tons, into another ladle and mixing it with a silicon compound.—W. R. S.

*Steel; Preventing the formation of poisonous dust during the hardening and tempering of—.* Verein. Schwarzfarben- und Chem. Werke, Akt.-Ges. Fr. Pat. 471,768, May 4, 1914.

HARDENING mixtures containing potassium cyanide, etc., are used in the form of small tablets, balls, or the like to prevent dusting.—W. E. F. P.

*Steel high in manganese; Process for rendering—easily machinable.* Poldhütte Tiegelgussstahlfabrik. Fr. Pat. 472,185, May 14, 1914. Under Int. Conv., May 27, 1913.

THE piece of steel is maintained between 350° and 800° C. for 1 hour or longer according to its size, and then allowed to cool.—W. E. F. P.

*Furnace for heating or annealing.* A. Smallwood, London. Eng. Pat. 4480, Feb. 20, 1914.

THE material under treatment is conveyed to and from the heating chamber upon a hollow carrier or truck heated internally by the gases from a portable fire-chamber, which may form part of the carrier. The heating gases pass from the fire-chamber through longitudinal and transverse flues within the carrier, provided with openings which can be controlled independently.—W. E. F. P.

*Crucible-furnace.* F. M. Her, Denver, Colo. U.S. Pat. 1,129,983, March 2, 1915. Date of appl., May 20, 1912.

IN a cylindrical furnace having an open top, a spiral air-heating flue is provided in the wall of the crucible chamber. Air is supplied to the upper

end of the flue from a pressure chamber at the base of the furnace, and discharged, heated, into the fuel duct at the lower part of the crucible chamber. The furnace is made in two sections to permit removal of the crucible.—W. E. F. P.

*Metallurgical furnace.* U. Wedge, Ardmore, Pa. U.S. Pat. 1,131,449, March 9, 1915. Date of appl., July 10, 1913.

A MULTIPLE-HEARTH furnace, with a central rotating shaft carrying rabble arms, and a valved passage through each hearth for permitting a flow of ore from an upper to a lower chamber whilst preventing upward flow of gas. The valves are operated at regular intervals by the arms carried by the shaft above the uppermost hearth.

—W. R. S.

*Furnaces; Cooling electric [smelting]—by air.* H. Magron, Fos, France. U.S. Pat. 1,131,009, March 9, 1915. Date of appl., Feb. 9, 1915.

COOLED air is circulated and expanded in contact with the walls of the furnace, to cool the outer portion of the charge below its melting point.

—B. N.

*Ores; Concentration of.* H. L. Sulman, and Minerals Separation Ltd., London. Eng. Pat. 4938, Feb. 25, 1914.

Is concentrating ores by flotation, e.g., by the agitation-froth process, a silicofluoride or hydrofluosilicic acid is added to the aqueous medium, in place of the sulphuric acid commonly used.

—W. E. F. P.

*Galvanising wire, sheets, and other products; Baths for.* N. K. Turnbull, Manchester. Eng. Pat. 5089, Feb. 27, 1914.

THE wire, etc., is galvanised continuously in a bath in which the molten zinc is supported on, and heated by molten lead. The tank is divided into compartments and by means of partitions a greater depth of zinc is maintained in the inlet and exit compartments than in the middle one, so that as dross is formed it descends out of the path of the material under treatment.—W. E. F. P.

*Cadmium from zinc ores; Removal of.* G. Rigg, Palmerton, Pa., Assignor to New Jersey Zinc Co., New York. U.S. Pat. 1,129,904, March 2, 1915. Date of appl., Dec. 3, 1914.

THE ore is roasted and the cadmium is then converted into sulphate by leaching with an aqueous solution of zinc sulphate; the zinc sulphate is derived in part directly from the roasted ore and in part by adding sulphuric acid to the leaching liquid. The roasted ore is added gradually to the leaching liquid, and the resulting liquid drawn off.—W. E. F. P.

*Tungsten powder; Process for producing.* R. Rafn, Porsgrund, Norway, Assignor to General Electric Co., Schenectady, N.Y. U.S. Pat. 1,130,197, March 2, 1915. Date of appl., Sept. 20, 1912.

TUNGSTEN trioxide is heated to dull redness in ammonia to produce the blue oxide, which is reduced to metal by heating in hydrogen at a higher temperature.—W. E. F. P.

*Aluminium alloy.* A. Wilm, Berlin. U.S. Pat. 1,130,785, March 9, 1915. Date of appl., July 31, 1911.

AN alloy of aluminium with Mg about 0.5, Cu not more than 6 (e.g., 3) and Mn not more than 3 (e.g., 1)%.—W. E. F. P.

*Aluminium and its alloys; Solder for.* G. Bendel. Fr. Pat. 471,641, March 17, 1914. Under Int. Conv., April 3, 1913.

AN alloy of Cd 13, Sn 1, and Zn 6 parts by weight. The surfaces to be joined are heated to the melting point of the solder, rubbed with the latter until good contact is effected, pressed together, and quenched while under pressure.—W. E. F. P.

*Aluminium; Low-temperature solder for.* L'Omnium des Industries Nouvelles. Fr. Pat. 472,393, May 19, 1914.

THE solder is prepared by adding 80 parts of tin, 10 of zinc, 5 of bismuth, and 5 of aluminium to molten potassium chloride, additions of the latter being made at intervals to bring the total quantity up to 30 parts; when the charge is at a cherry red heat, 4 parts of bismuth chloride is added and the mixture well stirred, poured, and allowed to cool. The solder can be used with a soldering iron.

—W. E. F. P.

*Ores; Plant for the reduction and smelting of.* E. D. Kendall, Elizabeth, N.J., Assignor to executors of J. B. Haggin. U.S. Pat. 1,131,709, March 16, 1915. Date of appl., July 14, 1914.

A SHAFT furnace, closed at the top, has within its walls a conduit for delivering ore and reducing agent to the crucible, and within the conduit a removable perforated pipe connected with an exhausting fan for the removal of the gases; the perforations are protected by hoods. Another similar conduit is provided for introducing a flux.

—W. R. S.

*Copper; Process of extracting.* C. H. Benedict, Lake Linden, Mich. U.S. Pat. 1,131,986, March 16, 1915. Date of appl., April 18, 1914.

COPPER-BEARING sands are leached successively with a series of cupric-ammonium salt solutions of decreasing strength; copper and ammonia are recovered from the strongest solution, and the weaker ones are used again for leaching.—W. R. S.

*Colloidal metal solutions; Manufacture of stable.* —, Ges. f. Elektro-osmose m. b. H. Fr. Pat. 471,679, April 10, 1914. Under Int. Conv., April 14, 1913.

COLLOIDAL metal solutions are stabilised by soluble silicic acid, especially that prepared as described in Fr. Pat. 471,678 (see page 423), a salt of the metal being added to the silicic acid solution and then reduced, preferably by hydrazine hydrate.

—F. Sodx.

*Iron alloy for dynamo-electric purposes; Process of manufacturing an.* W. Rübel, Berlin. U.S. Pat. 1,130,678, March 2, 1915. Date of appl., July 9, 1912.

SEE Addition of July 10, 1912, to Fr. Pat. 429,758 of 1911; this J., 1913, 116.

*Metals from low percentage ores; Process for extracting.* H. S. Mackay, Norwich, Conn., U.S.A. Eng. Pat. 26,138, Nov. 14, 1913.

SEE U.S. Pat. 1,094,371 of 1914; this J., 1914, 598.

*Sulphide ores; Concentration of.* Minerals Separation and De Bary's Processes Australia Proprietary, Ltd., Melbourne, Australia. Eng. Pat. 5856, March 7, 1914. Under Int. Conv., April 3, 1913.

SEE Fr. Pat. 469,677 of 1914; this J., 1915, 35.



*Magnetic separator.* G. Ullrich, Magdeburg, Assignor to F. Krupp Akt.-Ges., Grusonwerk, Magdeburg-Buckau, Germany. U.S. Pat. 1,130,648, March 2, 1915. Date of appl., Nov. 25, 1913.

SEE Fr. Pat. 464,156 of 1913; this J., 1914, 425.

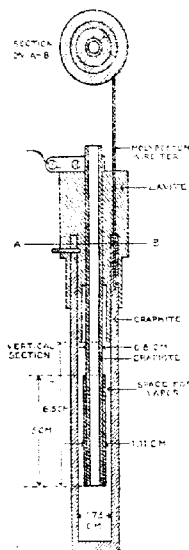
*Desulphurising ores; Process for —.* G. Fusina, Genoa, Italy. U.S. Pat. 1,131,691, March 16, 1915. Date of appl., April 25, 1912.

SEE Fr. Pat. 442,280 of 1912; this J., 1912, 931.

## XL.—ELECTRO-CHEMISTRY.

*Electrical conductivity above 1500° C. of vapours at normal pressure; Methods, data, and new apparatus for measuring —.* E. F. Northrup. J. Franklin Inst., 1915, 179, 337—352.

PRELIMINARY experiments showed the character of the electrical conduction of metallic vapours to depend upon the form (and probably the material) of the container, the applied voltage and its direction, the temperature, the nature of the metal, and the frequency when an alternating voltage was employed; and it was found necessary to make the measurements with direct e.m.f. which could be commutated, and then repeat them with alternating e.m.f. of different known frequencies. The vertical electric furnace employed had a cylindrical chamber, 2.2 cm. in diameter, and a heating length of 13 cm. An interchangeable heater-unit of graphite, employing a metal of very high m. pt. as resistor bearing a definite relation to the temperature of the furnace when the latter was heated slowly. The metal resistor was protected from oxidation by the gases (CO+N) developed in the furnace at red heat. To heat the furnace rapidly to 1500° C., about 1600 watts was required, and an equilibrium temperature of 1645° C. was attained in about 2½ hours, the maintenance of the latter requiring 28.6 volts and 58 amperes; in one test a heater-unit lasted for 137½ hours. The container for the vapour (see fig.), made of Acheson graphite, was held in position and insulated from the crucible by a piece of baked "lavite" which also formed a cover for the furnace chamber, the resistance measured being that of the hot vapour in the space between the outer surface of the inner cylinder and the inner surface of the cylindrical crucible, the internal diameter of which was 1.75 cm. The temperature to which the vapour might be raised was limited by the m. pt. of lavite (about 1525° C.). In using the apparatus, a small piece of the metal to be examined was placed in the bottom of the graphite crucible and the temperature of the furnace steadily increased (never being allowed to decrease while the measurement was in progress). Measurements were made of the conductivity of the crucible



gases (CO+N) from 900° to 1550° C., of the asymmetric resistance of the latter at 1510° C., and of the conductivity of mercury vapour from 900° to 1500° C.; but it is recognised that quantitative measurements as regards metallic vapours will be of little practical value until means are provided for maintaining the vapours under pressure; above 1200° C., minute particles of carbon (from the graphite container) are intermingled with the vapour or gas in the crucible, and these particles probably are largely responsible for the electrical conduction observed. Considering that the electrical conductivity found for all oxide powders and refractory materials might be due in part to the conductivity of the hot gases permeating the solid material, a container was packed full of very pure alumina, and the resistance (milliamperes vs. °C.) measured at 50 volts, the central electrode being maintained positive. From the results obtained, in conjunction with previous measurements, it was found that about 21% of the conductivity of the alumina was due to that of the hot gases in its interstices, and it is therefore concluded that at temperatures exceeding 1500° C. it is impossible to obtain even approximately good electrical insulation by any means.—W. E. F. P.

*Silver voltameter; Studies on the —.* G. A. Hulet and G. W. Vinal. J. Phys. Chem., 1915, 19, 173—192. (See also this J., 1914, 482; 1915, 91.)

COMPARATIVE tests made with porous cup voltameters employed at the U.S. Bureau of Standards and Princeton University, respectively, resulted in good agreement. Several kinds of porous cups were used, and the voltameters differed appreciably in size and shape. In making determinations of acidity to ascertain when the porous cups were in equilibrium with the electrolyte, methyl red was used as indicator in preference to iodocochin. In the final washing of the deposit with conductivity water the change of conductivity of the water is the best criterion of the efficiency of the washing, but the operation must be accomplished speedily, as owing to electrochemical action even conductivity water slowly dissolves silver which has been deposited on platinum.—J. R.

## PATENTS.

*Furnace; Electric arc —.* E. Troye and E. Edwin, Assignors to Norsk Hydro-Elektrisk Kvaestofaktieselskab, Christiania, Norway. U.S. Pat. 1,122,555, Dec. 29, 1914. Date of appl., June 26, 1914.

THE arcs are arranged in a multiphase star circuit, to render them stable, and a multiphase transformer is connected to the circuit, with an arc for each phase connection. A grounded metallic neutral connection, common to all the phase connections, is connected to the neutral point of the transformer, and switches are arranged in the metallic connections between the arcs and the neutral point. Each phase connection is provided with a reactance, tuned to pass only the first harmonic of the current. Different arrangements are described in which a furnace is in each phase connection of a three-phase transformer, and connected to a neutral wire, or with the furnaces in induction currents, or with several furnaces supplied with induced currents from the same primary winding, or in which choking coils are employed.—B. N.

*Furnace; Electric —.* J. Blatchford, Oak Park, Ill. U.S. Pat. 1,129,842, March 2, 1915. Date of appl., Aug. 19, 1914.

THE outer and inner walls of a horizontal tubular double-walled body portion are spaced apart by end pieces, each provided with a rib, projecting

backwards, which receives the walls on its outer and inner edges respectively. The inner wall forms a refractory core, and three heater resistance conductors are distributed uniformly upon its outer surface and embedded in cement; the space between the walls is filled with refractory packing material. The conductors are connected to a source of current and to three single-pole double-throw knife switches mounted on the furnace, so that the resistances may be connected in various ways, with relation to each other and to the source of current, to produce different temperatures. A door is arranged in one of the end pieces, and a plug, slotted diagonally and adapted to provide an adjustable vent, in the other.—B. N.

*Oven and kiln; Electrical*——. L. H. Giddings, Pasadena, Cal. U.S. Pat. 1,130,392, March 2, 1915. Date of appl., June 29, 1911. Renewed July 20, 1911.

The oven is provided with an inner and outer wall, the upper portion of the outer chamber between the walls forming an air compartment. Bridges are arranged in the outer chamber with electrical resistances on them, and air is admitted to the chambers through inlets which may be closed. Ports, at the top and bottom of the inner wall, connect the two chambers, and are controlled by plugs sliding in them. An outlet, below the levels of the ports, connects the inner chamber with a flue and stack, and means are provided "to yieldingly seal the outlet."—B. N.

*Furnace; Electric*——. W. S. Horry, Niagara Falls, Assignor to Union Carbide Co., New York. U.S. Pat. 1,130,734, March 9, 1915. Date of appl., Jan. 21, 1914.

MULTIPHASE current is supplied to several sets of electrodes, disposed symmetrically, by a number of conductors, arranged in parallel for each phase. Each of the electrodes receives current of different phase from that of neighbouring electrodes, and the conductors extend to the electrodes by different routes, each interlinked with others carrying current of opposing phase, whereby the self-induction of the system is minimised; each set of electrodes is connected in delta to its own supply.—B. N.

*Gases; Process for the synthesis of*——. [Electrical] process for producing reactions in gases and apparatus for practising the same, L. L. Summers, Chicago, Ill. U.S. Pats. (A) 1,130,940 and (B) 1,130,941, March 9, 1915. Date of appl., Nov. 25, 1911.

(A.) ONE or more of the constituent gases is strongly heated, and a relatively cool gas is then injected under pressure, whereby the gases are made to combine; the resulting gases are quickly removed from the heat zone. (B.) An arc is established, and the more inert gas is fed into the arc. A second gas is injected under pressure, thus extinguishing the arc, which is then immediately re-established.—B. N.

*Battery-separator and process of making the same*. J. M. Skinner, Assignor to Philadelphia Storage Battery Co., Philadelphia, Pa. U.S. Pat. 1,130,640, March 2, 1915. Date of appl., May 13, 1914.

THE wood of coniferous trees is shaped into the form of separators, and boiled in water for from 24 to 48 hours at atmospheric pressure. B. N.

*Ozone; [Electrical] apparatus for generating*——. W. J. Knox, New York, Assignor to Knox Terpezone Co. of America. U.S. Pat. 1,130,827, March 9, 1915. Date of appl., Dec. 1, 1910.

TWO concentric glass tubes are separated by an annular space closed at one end, one of the tubes

being roughened on the inner surface and forming a dielectric. A body of mercury in the annular space acts as the electrode, the metal entering the indentations of the roughened part, and forming a number of fine discharge points. B. N.

*Liquid; [Electrical] process of treating [separating suspended matter from]*——. C. P. Landreth, Philadelphia, Pa. U.S. Pat. 1,131,067, March 9, 1915. Date of appl., June 10, 1914.

SUSPENDED matter is separated by passing an electric current through the liquid to form a coagulant. A part of the deposited sediment and coagulant, separated by settling, may be again introduced into the liquid, subsequent to the electrical treatment.—B. N.

*Manufacture of soluble, chemically pure silicic acid*. Fr. Pat. 471,678. See VII.

*Influence of electricity upon plant growth*. Dorsey and Clements. See XVI.

## XII.—FATS; OILS; WAXES.

*Cotton-seed; Nitrogen and fat in short-staple*——. C. A. Wells and E. H. Smith. J. Ind. Eng. Chem., 1915, 7, 217.

SPECIMENS of eighteen varieties of upland short-staple cotton, grown on red clay soil which had been uniformly fertilised, were ground under uniform conditions in the same machine, and the remaining lint was removed from the seed by hand; the amount of lint not removed by the gin may vary from 97 to 124 lb. per 1000 lb. of seed. The moisture content of the kernels of these eighteen varieties ranged from 6.42 to 9.75%, the fat from 35.20 to 48.04%, and the nitrogen from 5.16 to 6.22%. Arranging the eighteen varieties in two groups of nine, according to the nitrogen content of the kernels, a ton of mixed cottonseed from one group would contain 8.3 lb. more nitrogen (value about 8s. 4d.) and 13.6 lb. less oil (value about 2s. 1d.) than a ton from the other group, leaving a balance of 6s. 3d. per ton in favour of the seed of high nitrogen content. The nine varieties in the high nitrogen group (N. 5.43–6.22; average 5.90%) were Schley, Pey's improved, Cook's improved, Jarman K. sunbeam, Willet's ideal, Cook's No. 675 Ala. Exp. Station, Wanamaker's ext. big boll—storm proof, King and triumph hybrid, and Hite's early prolific.—A. S.

*Unsaponifiable matter in greases; [Determination of]*——. E. Twitchell. J. Ind. Eng. Chem., 1915, 7, 217–218.

FIVE grams of the sample or, preferably, of the fatty acids prepared for the "titer" test, is saponified with alcoholic potash, and the mixture evaporated nearly to dryness, treated with a small quantity of alcohol and with water, and washed into a separating funnel; the volume of the soap solution should be 150–200 c.c., and the ratio of alcohol to water 1:4. The solution is shaken with two successive 50 c.c. portions of ether, and the united ether extracts are washed once with water, once with dilute hydrochloric acid, then again with water, transferred to a weighed dish, evaporated, and the residue dried at 110° C. and weighed. It is then dissolved in neutral alcohol and titrated with standard alkali; the quantity of fatty acids (derived from a small quantity of soap dissolved by the ether) thus found, calculated as oleic acid, is deducted from the weight of the original residue.—A. S.

*Emulsions; Experiments on*—. Adsorption of soap in the benzene-water interface. T. R. Briggs. J. Phys. Chem., 1915, 19, 210—231.

THE amount of sodium oleate removed from aqueous solution by emulsifying with benzene depends upon the specific surface of the benzene phase and the concentration of the soap solution; it increases rapidly at first with small increases of concentration, but subsequently is practically unaffected by large increases. The emulsification depends upon the formation of a viscous semi-solid film of soap about the benzene globules: the condensation of solute in the liquid interface is regarded as a special case of adsorption. Discrepant results were obtained with hand-shaken emulsions owing to the varying size of the benzene globules. Such emulsions were "homogenised" by impinging upon a baffle wall from an orifice of 0.5 mm. diam. at about 1 at. pressure: after eight or ten treatments most of the globules were reduced to less than 5 $\mu$  diam. The adsorption was then much more pronounced, and the stability of the emulsion was greatly enhanced. With a "homogenised" solution having a final equilibrium concentration of 0.36 grms. of sodium oleate per litre, the observed amount of oleate adsorbed by a litre of benzene was 0.44 grm., the amount calculated from Freundlich's adsorption equation being 0.42 grm.—J. R.

#### PATENTS.

*Oil or grease from animal or other matter; Extraction of*—. D. Adamson, Hyde. Eng. Pat. 5709, March 6, 1914.

THE material (fish refuse) is extracted in a rotating vessel by means of a volatile solvent, which is admitted through a passage in the trunnions, whilst the extract is drawn off through a grid covered with filtering material. Steam may be supplied to a coil within the vessel through another passage in the trunnions.—C. A. M.

*Oils; Mixing device for use in the hydrogenation of*— and in similar processes. G. Calvert, London. Eng. Pat. 5967, March 9, 1914.

THE mixture of oil and catalyst is treated with hydrogen in a closed vessel containing a rotating comb-shaped agitator surrounded by a stationary gauze screen, which finely subdivides the oil, whilst a centrifugal propeller at the base flings the mixture upwards to be beaten and subdivided again. Hydrogenation is accelerated by the impact of the oil against the screen.—C. A. M.

*Fatty matter; Hydrogenising*—. F. W. de Jahn, New York. U.S. Pat. 1,131,339, March 9, 1915. Date of appl., April 1, 1913.

THE finely-divided fat is agitated with hydrogen in one vessel and then passed through a second vessel containing the catalyst. Air is withdrawn from both vessels, and the circulation of the fat continued until hydrogenation is complete.—C. A. M.

*Fats; Apparatus for the catalytic hydrogenation of*—. R. P. Pictet. Fr. Pat. 472,080, July 24, 1913.

THE oil, with or without the addition of a catalyst, is made to pass by gravitation through a series of communicating tubes the walls of which are composed of a catalytic metal. The inner surface of the walls of the tubes is submitted to a preliminary treatment to increase the catalytic activity of the metal. Hydrogen in suitable proportion is introduced into the tubes, and the oil is subdivided by rotating devices, which constantly brush against the inner walls.—C. A. M.

*Oils; Process of refining animal and vegetable*—. C. Baskerville, New York. U.S. Pat. 1,130,698, March 9, 1915. Date of appl., March 13, 1914.

THE oil, e.g., cottonseed oil, is neutralised with caustic alkali, with or without the addition of a saline electrolyte, the alkali soap dehydrated by heating with an anhydrous salt (e.g., sodium carbonate), and the coagulum separated.—C. A. M.

[Fullers'] earth-treating process. M. J. Welsh, Assignor to The Atlantic Refining Co., Philadelphia, Pa. U.S. Pat. 1,132,054, March 16, 1915. Date of appl., June 7, 1913.

FULLERS' earth which has been used to treat oily liquids, is revived by treating it with a suitable solvent, or calcining it, and then treating it with acid, which removes the ingredients "tending to produce fusion."—A. B. S.

*Detergents; Preparation of stable oxygenated*—. H. Siebold. Ger. Pat. 279,306, April 23, 1913.

A PERPHOSPHATE is mixed with soap or other detergent material. The products are more stable than perborate preparations.—A. S.

*Washing and bleaching of wool, and recovery of grease and potassium salts*. Fr. Pat. 471,651. See V.

#### XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

*Granular substances [pigments, etc.]; Valuation of*— by counting the particles. C. Kühn. Z. angew. Chem., 1915, 28, 126—128.

FROM 0.1 to 0.5 grm. of the powder is shaken for 15 mins. with a suitable distributing medium (turpentine, linseed oil, glycerol, water) in a 10 c.c. brass cylinder, and 0.01 c.c. of the homogeneous mixture is withdrawn with a micro-pipette, diluted to 1 c.c. with the liquid, and again shaken for 15 mins. One drop is then placed on the object glass of a Zeiss-Thoma chamber for counting the corpuscles in blood, covered with the cover-glass, and the number of particles counted (after 1 to 12 hours) under a magnification of 550 diam. Duplicate results should agree within 4%. The method affords a criterion of the fineness of ground and precipitated products, such as flour, pigments, oil-paints, etc., and may be used in the examination of explosives. For example, 1 grm. of heavy spar contained the following number of particles:—Once ground, 4.5; twice ground, 12; and thrice ground 18.4 milliards. One grm. of lamp black (sp. gr. 1.57) contained 960 milliards of particles: an average particle thus weighed  $1.04 \times 10^{-12}$  grm., had a diam. of 1.08 $\mu$ , and contained 26 milliard mols. of carbon.—C. A. M.

*Paints to prevent electrolysis [of iron and steel] in concrete structures*. H. A. Gardner. J. Franklin Inst., 1915, 179, 313—336.

AS the result of an investigation to ascertain the best type of paint for insulating iron, etc., when embedded in concrete (thereby inhibiting the corrosion caused by the action of stray currents of electricity), it was concluded that the vehicle of the paint should contain boiled or bodied oils or products which dry—by polymerisation rather than oxidation—to a fairly saturated film having a dull rather than a glossy surface; that the solid portion of the paint should contain a percentage of pigments which are inert, electrically non-conducting, and coarse (so as to produce a film

having a rough surface), and also pigments of the basic or chromate type; and that, if possible, sand should be applied to the painted surface whilst it is still tacky, to improve the adhesion of the cement or concrete.—W. E. F. P.

*Linseed oil treated with cobalt, lead, and manganese oleostearates; Drying properties of*—L. E. Wise and R. A. Duncan. *J. Ind. Eng. Chem.*, 1915, 7, 202—205.

An aqueous solution of the potassium soap of Chinese wood oil was treated with solutions of lead acetate, manganous chloride, and cobaltous chloride respectively, and the precipitated soaps were filtered off, washed with water, and dried *in vacuo* over fused calcium chloride: the lead soap contained 28% Pb, the manganese soap 10% Mn, and the cobalt soap 9% Co. The effect of equivalent quantities of these soaps on the drying of linseed oil under identical conditions was studied, comparative tests with litharge being made at the same time. The oil containing the manganese soap dried most rapidly and showed the lowest maximum gain in weight. The lead soap gave results very similar to those obtained with litharge, except that there was a somewhat greater gain in weight during the first stage of the drying. The effect of the cobalt soap was similar to that of the lead soap, but the film lost weight more rapidly after the maximum gain in weight had been attained.—A. S.

*Floor polishes; Examination of*—A. A. Besson and R. Jungkunz. *Chem.-Zeit.*, 1914, 38, 1141—1142; 1173—1175; 1182—1185.

Floor polishes usually consist of a mixture of wax and turpentine or turpentine substitutes (petroleum products); some contain benzene. The solvent is separated by steam distillation, and the residue submitted to the ordinary methods of wax analysis in order to ascertain its composition. The oily portion of the distillate is separated from the water, and its specific gravity, refraction, iodine value, boiling point, ignition point, and flash point are determined. Whilst turpentine ignites at 31.7°—35.2° C., petroleum products used as turpentine substitutes ignite at 24.2°—28.7° C., and naphtha and benzene burn at ordinary temperatures. Many of the turpentine substitutes have an iodine value of less than 15. The polymerisation test described by Eibner and Hue (this J., 1910, 890) is useful for the determination of the amount of turpentine substitutes present, but Sangajol behaves like turpentine with the test. The refractometer value of turpentine is 60—72, of Sangajol, 81, and of other substitutes, less than 30. In the case of mixtures such as the above, fractional distillation must be carried out under definite conditions to obtain any useful data; the point at which the product commences to boil affords some indication of the nature of the solvent. In the case of turpentine this point is 156° C.; for Sangajol it is 95°—104° C., and for other substitutes 133°—145° C.—W. P. S.

#### PATENTS.

*Anti-corrosive composition.* G. Carter, Leeds. Eng. Pat. 22,533, Nov. 14, 1914.

A PREPARATION for preventing the rusting of machinery, etc., is obtained by dissolving resin (100 oz.) in hot petroleum spirit (100 oz.), adding a liquid drier (5 oz.) and "solid spirit-soluble red" ( $\frac{1}{4}$  to  $\frac{1}{2}$  dr.), and, when cold, straining the liquid.—C. A. M.

*White pigment; Method of making a*—H. W. Kessler, Assignor to The Kessler Co., Cleveland, Ohio. U.S. Pat. 1,131,144, Mar. 9, 1915. Date of appl., Dec. 22, 1909.

A COMBUSTIBLE mixture of powdered metallic lead, air, and a gaseous hydrocarbon fuel is ignited and introduced into an atmosphere of carbon dioxide, with or without admixed steam, and the resulting carbonate is separated from the gases.—C. A. M.

*Turpentine-distilling apparatus.* H. E. Bryant, Assignor to American Patent Manufacturing Co., Jacksonville, Fla. U.S. Pat. 1,130,743, Mar. 9, 1915. Date of appl., Sept. 5, 1911.

THE products of the distillation are collected in a separating chamber surrounded by a cooling tank and the turpentine is drawn off into a receiver, also within the cooling tank, means being provided for watching the distillation and taking samples of the distillate.—C. A. M.

*Varnishes and other like materials and process for producing same.* A. B. and F. P. Walker, Assignors to W. R. Wood, Cincinnati, Ohio. U.S. Pat. 1,131,578, Mar. 9, 1915. Date of appl., Oct. 31, 1910.

A VARNISH free from organic resins or gums, is composed of a solution of aluminium soap and an oxide of an alkaline earth metal diluted with a suitable "carrier."—C. A. M.

*Furfural; Use of*—in the manufacture of varnish resins. G. Meunier. Fr. Pat. 472,384, Aug. 2, 1913.

RESINOUS products, suitable for varnish making, are obtained by heating furfural alone or in admixture with ketones or aldehydes, in the presence of an inorganic or organic base, either at atmospheric or increased pressure. For example, aniline heated with an equal volume of furfural in a closed vessel for 48 hours at 70° to 80° C. yields a black resinous compound soluble in benzene. A yellow resin may be obtained by heating a mixture of furfural and acetone with an aqueous solution of sodium hydroxide beneath a reflux condenser.—C. A. M.

*Resin oil; Process of manufacturing pure*—M. Melamid, Freiburg, Germany. U.S. Pat. 1,131,939, March 16, 1915. Date of appl., June 10, 1913.

SEE Eng. Pat. 9852 of 1912; this J., 1913, 820.

*Production of tar oils which may be used as paint oils and with increased antiseptic and fungicidal properties.* Fr. Pat. 471,671. See III.

*Cleaning and disinfecting liquids.* [Paint remover. Fr. Pat. 471,717. See XIXc.

#### XIV.—INDIA-RUBBER; GUTTA-PERCHA.

*Rubber and latex: The proteins in*—F. Frank. Rubber Industry, London, 1914, 144—148.

THE following process for the estimation of the total insoluble proteins in rubber has given uniform results in the hands of different workers:—1 to 2 grms. of raw rubber is heated in a test-tube, 30 mm. diam., with 30 c.c. of boiling cymene, limonene, or dipentene until a thin, homogeneous solution is formed. The tube is then run in a centrifugal machine at 2500—3000 revs. per minute, for 1 to 1½ hours, the clear solution is poured off, and the residue is boiled with xylene and again separated by centrifuging. The process

is repeated with benzene, and again with ether, after which the residue is dried and weighed. The separation is not quite quantitative, but the proportion lost is constant. The protein is not decomposed by the process of separation. It gives the biuret, xanthoproteic, lead sulphide, and Millon's reactions. Liebermann's reaction is uncertain, but the product gives all precipitation reactions characteristic of albumins. For the products of hydrolysis, see this J., 1915, 187. From a technical point of view it appears desirable so to manage the coagulation of the latex that the albumins remaining with the rubber may be present in a form which is not liable to disintegration. (See Eng. Pat. 22,255 of 1912; this J., 1913, 298.)—E. W. L.

*Rubber latex; Chemical coagulation of*—E. Kaye. Rubber Industry, London, 1914, 137—143. (See also this J., 1913, 760.)

THE amount of phosphorus present in samples of *Hevea* rubber prepared by different processes varies considerably; in Fine Hard Para from various sources the amount is fairly constant. For example, the amount of phosphorus (as  $P_2O_5$ ) in a sample of Pale Plantation Crêpe was 0.035; in Best Smoked Sheet (unwashed), 0.092; in "Byrne Process" Rubber (unwashed), 0.162; in four samples of Fine Hard Para, 0.0520, 0.0805, 0.0624 and 0.0620%, respectively, calculated on the rubber. Study of the quality and nature of the phosphorus in the latex would probably help to elucidate the chemical character of the changes taking place in the protein components during coagulation under the influence of enzymes, dilution with water, and acid- or alkali-hydrolysis.

—E. W. L.

*Rubber; A study of some recent methods for the determination of total sulphur in*—J. B. Tuttle and A. Isaacs. U.S. Bureau of Standards, J. Franklin Inst., 1915, 179, 353—354.

THE direct solution methods of Spence and Young (this J., 1912, 651), and Deussen (this J., 1913, 951), involving the use of concentrated nitric acid, were found to give low results; and the direct fusion methods of Alexander. The Joint Rubber Insulation Committee (this J., 1914, 150), and Kaye and Sharp, and the solution and fusion method of Frank and Marekwald, were reliable only with rubber having a low content of free sulphur. The most satisfactory results were obtained by the method of Waters and Tuttle (this J., 1911, 1268). It is suggested that separate determinations be made of the free sulphur and that remaining after extraction, and the sum of these reported as the total sulphur.—W. E. F. P.

*Crystalline compound of isoprene with sulphur dioxide*, De Bruin. See XX.

#### PATENTS.

*Vulcanised india-rubber goods; Manufacture of*—W. E. Muntz, London. Eng. Pat. 4955, Feb. 25, 1914.

THE fabric in vulcanised rubber goods is preserved from attack by sulphurous and sulphuric acids formed by oxidation of free sulphur, by (1) adding to the mixing, or impregnating the fabric with, additive compounds of ammonia with certain salts, e.g., zinc sulphate ( $ZnSO_4 \cdot 5NH_3$ ) or magnesium sulphate ( $MgSO_4 \cdot 5NH_3$ ); or forming such compounds *in situ* by first adding the salts to the mixing or fabric, and then treating the goods, before, during, or after vulcanisation, with ammonia; (2) adding to the mixing, or impregnating the fabric with, acetic acid or other organic acids, subsequently treating the goods with liquid or gaseous ammonia or other alkali; (3) applying to

the goods, either together or successively, ammonia and carbon dioxide, in the proportion of 2 vols. to 1 vol., preferably under pressure in a closed vessel.—E. W. L.

*Rubber goods; Process of and apparatus for vulcanising*—P. M. Matthew, Edinburgh, Eng. Pat. 5164, March 3, 1914.

RUBBER sheeting, inserting, belting, etc., is vulcanised by leading it continuously in a sinuous path around and between the surfaces of heated rotating cylinders. To obtain a highly polished surface the members of one or more pairs of cylinders may be caused to rotate at different speeds. A pattern may be applied to the rubber by using engraved rollers.—E. W. L.

*Rubber and rubber-like substances; Process for accelerating the vulcanisation of natural and artificial*—S. J. Peachey, Stockport, Eng. Pat. 7370, March 24, 1914.

VULCANISATION is accelerated by adding to the mixing, before vulcanisation, a compound resulting from the interaction of an aromatic amine with an aliphatic or aromatic aldehyde, or of an aromatic aldehyde with ammonia. For example a mixing consisting of *Hevea* rubber, 100 parts, sulphur, 10 parts, and formaldehyde-aniline (or benzylidene-aniline) 1 part by weight, can be vulcanised in 40 minutes at 140° C. Hydrobenzamide is also mentioned as a suitable accelerator.—E. W. L.

*Rubber and rubber-like substances; Process for accelerating the vulcanisation of natural and artificial*—S. J. Peachey, Stockport, Eng. Pat. 10,833, May 2, 1914. Addition to Eng. Pat. 4263, Feb. 19, 1914 (this J., 1915, 368).

VULCANISATION may be accelerated by adding to the mixing *p*-nitrosodiphenylamine, or a reduction product of the nitroso-compounds named in the prior specification, e.g., dimethyl-*p*-phenylenediamine.—E. W. L.

*Rubber; Process for accelerating the vulcanisation of natural or synthetic*—Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 280,198, Jan. 1, 1914.

BASES or basic ammonia derivatives having a dissociation constant greater than about  $1 \times 10^{-7}$ , are added to the mixture before vulcanisation. Suitable substances are *p*-phenylenediamine, aldehyde-ammonia, benzylamine, naphthylenediamine, ammonium borate, and sodium-amide. The process is applicable to the product obtained by Kondakov by polymerisation of  $\beta\gamma$ -dimethylbutadiene.—A. S.

*Caoutchouc-like substances; Process for improving synthetic*—Badische Anilin und Soda Fabrik. Ger. Pat. 279,780, Jan. 10, 1914.

SYNTHETIC caoutchouc-like substances which are entirely or partly insoluble or sparingly soluble in benzene, are treated with organic acids or acid derivatives, with the exception of acids or derivatives in which the carboxy group is attached directly to a ring. The process is applicable, for example, to the products obtained from butadienes by polymerisation with alkali metals in presence of carbon dioxide or by autopolymerisation, or to those obtained by heating synthetic caoutchouc-like substances at ordinary or diminished pressure (see Eng. Pat. 975 of 1913; this J., 1914, 93).—A. S.

*Indiarubber and ebonite goods; Process of manufacturing*—from old or waste vulcanised rubber. H. Gare, Wembley. Eng. Pat. 10,030, April 23, 1914.

WASTE rubber is ground to a paste with water or other inert liquid and moulded, the fluid expressed

or evaporated, and the mass vulcanised or reformed by heating. Colouring, bleaching, or tanning agents, etc., may be added.—C. A. M.

*Vulcanised rubber; Process for separating — from fabric, metal particles, and other foreign substances. Process of regenerating vulcanised rubber.* J. Frydman, Fr. Pats. (A) 471,913 and (B) 471,996, July 22 and 23, 1913.

(A). VULCANISED rubber waste (100 kilos.) containing fabric insertion, metal particles, etc., is soaked for several hours at the ordinary temperature in 200 kilos. of the fraction of b. pt. 140°–170° C., obtained from certain petroleum distillates from the Dutch Indies, in particular that known as "Sangajol." The rubber is thus converted into a friable colloidal gel and can be readily separated from the fabric, etc. The fabric may then be subjected to successive hot extractions with the same solvent to recover the high-grade rubber with which, in the case of a tyre cover, it is impregnated, and to cleanse the fabric for further use. (B). Vulcanised rubber is heated at 140° C. in an autoclave, or in a vessel fitted with a reflux condenser, with the fraction of b. pt. 140°–170° C. from "Sangajol." The rubber and most of the organic constituents of the vulcanised rubber, as well as the sulphur, pass into solution, and are separated from the insoluble constituents by centrifuging. The rubber is then precipitated by the addition of ethyl or amyl alcohol or acetone, and is freed from the hydrocarbon solvent by washing or digesting with the precipitant and drying *in vacuo*.—E. W. L.

*Materials impregnated with rubber mixtures; Preparation of —.* W. Golombek. Ger. Pat. 278,717, Aug. 15, 1913.

THE emulsion of regenerated rubber, rubber solvent, and water, formed as an intermediate product in the regeneration of rubber, is used as an impregnating agent, either alone or in conjunction with raw rubber.—A. S.

*Caoutchouc; Production of vulcanised synthetic —.* F. Hofmann and K. Gottlob, Elberfeld, Germany, Assignors to Synthetic Patents Co., New York. U.S. Pat. 1,130,903, March 9, 1915. Date of appl., Oct. 16, 1913.

SEE Ger. Pat. 268,947 of 1913; this J., 1914, 365.

## XV.—LEATHER; BONE; HORN; GLUE.

*Tanning materials and cellulose extract in leather; Distinction and detection of —.* R. Lauffman. Ledertechn. Rundschau, Dec. 21 and 31, 1914. J. Amer. Leather Chem. Assoc., 1915, 10, 160–165.

SAMPLES of leather made with quebracho and chestnut extracts, with mixtures of these extracts, and with mixtures of quebracho extract with mangrove extract and with sulphite-cellulose extract, were dried, ground, and extracted with water. The aqueous infusions of leathers tanned with quebracho and with chestnut extracts, when tested by the usual methods, gave results similar to those given by the extracts themselves, whilst the infusion from leather tanned with a mixture of these extracts gave results more nearly resembling those obtained with chestnut extract, unless the leather was first partly tanned with chestnut and the tannage completed with quebracho. The infusion from leather tanned with a mixture of equal parts of quebracho and sulphite-cellulose extracts contained these in nearly equal amounts,

whilst that from leather tanned partly with quebracho and completed with sulphite-cellulose extract more nearly resembled the latter, the reverse being the case when the mixed tannage was carried out in the reverse order. In general, when leather is tanned partly with one extract and the tannage completed with another, the aqueous infusion more nearly resembles the latter, but a part of the tannin in all cases may be so firmly combined with the hide fibre that it does not appear in the aqueous infusion. Leathers containing sulphite-cellulose extract, in which this material can be detected immediately after tannage, may show no reaction when tested after three months.—T. C.

*Tannery effluents; Purification of — and recovery of by-products.* F. P. Veitch. J. Amer. Leather Chem. Assoc., 1915, 10, 126–141.

TANNERY effluents should always be subjected to sedimentation, with or without the addition of alum, before filtering. Lime mud should be kept separate from all other waste and the clear liquid mixed with the rest of the effluent after settling. The liquid is allowed to settle until the suspended matter is not more than 300 parts per million, and passed through a trickling filter not less than 6 ft. deep, the rate of flow being not more than 2 million gallons per acre per 24 hours. The effluent from the trickling filter is rarely satisfactory and must be further purified by sedimentation, by filtering through spent bark or sand, or by treatment with hypochlorite at the rate of 5 to 10 parts of chlorine per million. The approximate area, cost, and capacity of works capable of treating 1,000,000 gallons of effluent per 24 hours are given in the following table:—

	Area.	Capacity in galls.	Cost (in dollars)
Settling tanks.....	5000 sq. ft.	150,000 to 200,000	8000 to 15,000
Filter presses for sludge ..	—	—	1000
Rotary dryers .....	—	—	2500 to 3000
Sprinkling filters (9 ft.) ...	1 acre	—	22,000 to 37,000
Final settling tanks .....	1000 to 2000 sq. ft.	75,000 to 100,000	5000 to 10,000
Hypochlorite treatment ..	400 sq. ft.	—	1000

The dry sludges obtained from tannery effluents vary considerably in composition, containing nitrogen, 0.8 to 8.0%; phosphoric acid, 0 to 0.8; volatile matter, 20 to 85; ash, 14 to 60; lime, 0.5 to 35; fat, 0 to 14; chromium oxide, 0 to 1; arsenic, 0 to 7%. The value of the dried sludge is increased by keeping the waste lime separate from other wastes. The volume of effluent from tanneries is usually unnecessarily large, and it is generally possible to reduce it to about 100 galls. per day per hide without detrimental effect on the finished leather, with consequent cheapening of purification.—T. C.

*Waste products of agricultural interest — wool and leather wastes.* Russell. See XVI.

### PATENTS.

*Tanning of bulls or hides, and apparatus to be used therefor.* E. Wilson, Boutle. Eng. Pat. 7562, Mar. 27, 1914.

BUTTS or hides are kept in constant motion during tannage and the strength of the liquor is maintained throughout. The apparatus consists of a drum composed of an inner and outer frame, with an annular space, in which the hides are suspended

from sticks forming a skeleton or open periphery to the drum, which rotates in tanning liquor contained in a semi-cylindrical vat. An adjustable automatic feed supplies fresh liquor to the vat, which is provided with an adjustable overflow orifice.—F. C. T.

*Tanning products; Manufacture of* ——. Deutsch-Koloniale Gerb- und Farbstoff-Ges. Fr. Pat. 471,924, May 7, 1914.

FORMALDEHYDE (1 or 2 mols.), or a substance capable of yielding it, is condensed in aqueous solution with 2 mols. of  $\alpha$ - or  $\beta$ -naphtholmonosulphonic acid, or heteronuclear  $\alpha$ - or  $\beta$ -naphthylaminomonsulphonic acid. Mixtures or salts of these acids may be used. The products may be used in conjunction with vegetable tannins.—F. C. T.

*Sheep-skins; Preservation of — during unhairing (sweating) of fresh or dry pelt, and recovery of ammonia.* Soc. M. et A. Gasc. Fr. Pat. 471,966, May 8, 1914.

THE skins are treated with very dilute sulphurous acid before sweating. Sulphur dioxide is also mixed with the air entering the sweating chamber as soon as sufficient fermentation has taken place; the gases leaving the chamber are aspirated through a bath of dilute acid to recover ammonia. Fresh or dry pelt is washed in cold water and then treated with a solution of sodium sulphide, sulphurous acid, or common salt.—F. C. T.

*Leather-board, and process of producing the same.* A. L. Clapp, Braintree, Assignor to Hide-It Leather Co., Boston, Mass. U.S. Pat. 1,131,039, March 9, 1915. Date of appl., Jan. 11, 1913.

LEATHER-BOARD stock is prepared from comminuted dry chrome leather scrap by beating it out in presence of tannic acid, or of ordinary tanned leather scrap, or of some other reagent capable of converting the chrome salts, and finally alum is added to precipitate the soluble matters present.—E. W. L.

*Casein; Manufacture of plastic masses from* ——. Soc. anon. L'Oyonnaxienne. Fr. Pat. 472,192, May 14, 1914.

PLASTIC masses are obtained from casein by the addition, in varying proportions, of amines, amides, or their derivatives (e.g., aniline, acetanilide). The products can be kneaded, sheeted, pressed, sliced, or drawn into tubes or rods in the same manner and with the same plant as celluloid.—F. Sp.

## XVI.—SOILS; FERTILISERS.

*Ammonia in soils; Determination of* ——. R. S. Potter and R. S. Snyder. J. Ind. Eng. Chem., 1915, 7, 221—226.

EXISTING methods for the determination of ammonia in soils were found to be unsatisfactory. Good results were obtained by the application of Folin's aeration method of determining ammonia in urine (Z. physiol. Chem., 1902, 37, 161; see also Kober, J. Amer. Chem. Soc., 1913, 35, 1594): 25 grms. of soil is treated with 50 c.c. of water and a few drops of a heavy oil to prevent foaming, in a 500 c.c. Kjeldahl flask connected with a 16 oz. absorption bottle which, in turn, is connected with a pump. A current of air is drawn through the apparatus, the inlet tube reaching to within  $\frac{1}{2}$  in. of the bottom of the flask. About 2 grms. of sodium carbonate is added to the mixture

in the flask, and the liberated ammonia is absorbed in water to which 10 c.c. of N/10 sulphuric acid is added; in the subsequent titration alizarin red is used as indicator. Using an air current of 250 litres per hour no appreciable quantity of ammonia is carried over after 15 hours. The results are concordant, and if an ammonium salt be added to the soil, the whole of its ammonia is recovered in the subsequent determination. Methods based on extraction of the soil with hydrochloric acid give higher, and direct distillation with magnesia gives lower results than the aeration method.—A. S.

*Soil carbonates; Determination of* ——. W. H. MacIntire and L. G. Willis. J. Ind. Eng. Chem., 1915, 7, 227—228.

THE method described by the authors (this J., 1915, 93) for the decomposition of soil carbonates by phosphoric acid (1:15), did not give satisfactory results with a soil containing 5.2% carbonates calculated as  $\text{CaCO}_3$  and in which magnesium carbonate was probably present. They recommend, therefore, that hydrochloric acid (1:10) be used instead of phosphoric acid for miscellaneous work; this has no appreciable action on soil organic matter at the ordinary temperature. The carbon dioxide is absorbed in a 4% solution of caustic soda in a tower packed with beads, and determined by the double titration method of Amos (J. Agric. Sci., 1907, 1, 322), i.e., by using first phenolphthalein and then methyl orange as indicator.—A. S.

*Soil bacteria; Influence of protozoa upon* ——. T. Goodey. Roy. Soc. Proc., 1915, B 88, 437—456.

EXPERIMENTS were made with three soils from Rothamsted: A had been stored since 1816 and contained no protozoa; B dated from 1870 and contained amoebae and flagellates, but no ciliates; C was a fresh field soil (Hoosfield). After moistening with water, the bacterial content of B became much greater than that of A. When A was inoculated with soil bacteria, their number increased enormously up to 32 days, but then rapidly declined to, and remained lower than, the number present in untreated soil over 300 days. The presence of protozoa did not influence the bacterial content. In presence of vorticelli the number of organisms began to diminish after 63 days, and then kept at about the same level as in the untreated soil; the number in A alone showed marked diminution after 181 days. When soil A was inoculated with cultures of amoebae and of flagellates, both obtained from soil B, the bacterial content was well above that of untreated soil, and this remained true even when amoebae were present in very large numbers and under conditions favourable to their active growth. The number of organisms in soil A was greater, up to 232 days, than that in A treated with 10% of B, but thereafter they were approximately equal, and after 519 days the treated soil contained the most. A comparison of the organisms in C alone, in C treated with toluene, in C treated with toluene and then inoculated with protozoa, showed that the number was lowest of all in the first case, and much lower in the second case than in the third. After 487 days the inoculated soils were tested and the presence of protozoa established. The general conclusion is drawn that the hypothesis of Russell and Hutchinson (this J., 1909, 1213) that protozoa act as a factor limiting soil fertility by destroying nitrifying and other bacteria, is unwarranted so far as the forms of protozoa mentioned are concerned, and the results strengthen the author's previously expressed view (see this J., 1912, 243) that the ciliated protozoa exist in the soil in an encysted, inactive condition.—E. H. T.

*Plant growth; Influence of electricity upon* —. H. G. Dorsey and F. O. Clements. *Electrotechn. Zeit.*, 1914, 9, 236. *Chem.-Zeit.*, 1915, 39, Rep., 5.

GREENHOUSE experiments on the effect of electricity and of different kinds of lamp-radiations upon radishes and lettuce, showed that high-frequency currents were the most stimulating, and that direct and alternating currents, passed between electrodes sunk in the soil, were entirely without effect.—E. H. T.

*Gram plant, Cicer arietinum; Acid secretion of the* —. D. L. Sahasrabudhe. *Agric. Research Inst.*, Pusa, 1914, Bull. No. 45. 12 pages.

GRAM is the most common of all Indian pulse crops, covering an area of 13 million acres. It exudes an acid secretion through hairs present on every part, and this is washed off with a wet cloth and used medicinally. The secretion contains malic and oxalic acids in the proportion of 19:1. The acidity rises considerably at the flowering period, attains a maximum when the pods are fully developed, and then rapidly decreases as they become ripe. Pruning has no effect on the relative proportions of the two acids, but it increases their total amount. The secretion is a continuous process, and the amount normally found on the plant is a week's yield. The maximum yield of acid is obtained when the plants are washed every six days. An acre of gram produces nearly 6 lb. of malic acid, of which the cost of collection is 14 rupees (18s. 8d.).—E. H. T.

*Waste products of agricultural interest—wool and leather wastes.* E. J. Russell. *J. Board Agric.*, 1915, 21, 1087—1092.

MIDDLE-GRADE shoddies, containing 5–10% N, have long been used for fruit and hop farming, especially on the lighter soils. Experiments at Rothamsted have shown that they are also good for ordinary farm crops, and on heavy soils. The main effect is produced in the first year, but the residual value persists for another year or two. Shoddy is one of the cheapest nitrogenous manures on the market; it sells at 4s.—5s. per unit of nitrogen at the Yorkshire mills; in the south, transport charges increase the price to 7s.—8s. "Processed" shoddies, which have been treated with sulphuric acid or freed from oil, are of no more value than the untreated material. Untreated leather waste has no manurial value, but experiments with scrap that has been roasted or treated with sulphuric acid have given promising results. Untanned leather and scrap derived from the glove-making industry, have been proved to possess marked fertilising value.—E. H. T.

#### PATENTS.

*Superphosphate; Tiltting reaction chamber for* —. H. W. Hall, Zürich, Switzerland. *Eng. Pat.* 22,645, Nov. 17, 1914.

THE reaction chamber consists of an iron cylinder, lined with masonry, prepared wood, or superphosphate, mounted upon bearings so that its axis can be tilted from the horizontal. The cylinder has an opening in the top to admit the mixture and to draw off the reaction gases to the ventilating flue, and a slit in the bottom through which the material detached by a cutter falls into a conveyor below. Under the slit and fixed to the cylinder are runways for the cutting machine, which are protected from the falling superphosphate. The slit and ends are suitably closed before filling and the covers removed when the mass has set. The cylinder is then tilted back and the revolving cutter, worked by a motor, advances down the inclined runway against the superphosphate by the component of its own weight. When

the whole is excavated the cutter runs out at the back, or the cylinder is tilted forward and the machine travels out on to a trolley.—W. H. H. N.

*Phosphate compounds for manures and fertilisers; Manufacture of* —. A. Dickson, Dublin. U.S. Pat. 1,132,171, March 16, 1915. Date of appl., Sept. 12, 1914.

SEE *Eng. Pat.* 18,999 of 1913; this J., 1914, 1067.

#### XVII.—SUGARS; STARCHES; GUMS.

*Beetroots; Gummy malady of* —. G. Arnaud. *Comptes rend.*, 1915, 160, 350—352.

SOME beetroots taken recently from silos in two districts of Northern France had become gummy as the result of bacterial action. The flesh of the roots was somewhat translucent owing to the bacteria partially dissolving the cells and filling the intercellular spaces with a colourless viscous fluid. The affected roots first exhibited translucent spots on the surface; these afterwards extended to the interior, and cavities were produced in the parenchyma adjacent to the bast fibres. In the worst cases the roots acquired a hard spongy consistence, but the interior did not become brown nor was there any offensive odour. The bacterium responsible somewhat resembled the *B. Mori* of Murier, and developed rapidly in beet juice at 38°–40° C., producing fine regular filaments; some of these showed no trace of segmentation even after staining with magenta, but others gradually became transformed into chains of isolated elements varying in length from 1 to 10 diameters. In some cases these chains closely resembled those of *Leuconostoc mesenteroides*, but there were always some filaments present, although these were rare in the viscous fluid which exuded spontaneously from the infected roots. The infected roots had probably been injured by cold, for it was found impossible to communicate the malady to sound roots. From the industrial point of view the malady is objectionable in that it causes inversion of the sucrose and gives rise to a gum which is difficult to eliminate.—J. H. L.

*Sucrose; Inversion of* —. *Studies in catalysis. Part II.* A. Lambie and W. C. McC. Lewis. *Chem. Soc. Trans.*, 1915, 107, 233—248.

THE rate of inversion of sucrose by hydrochloric acid of varying concentration at 25°, 35°, and 45° C. was measured, and the values of the temperature-coefficients and their change with the concentrations of the catalyst were determined. It is shown that there is a slight fall in the critical increment (the extra amount of energy required to render 1 gm.-mol. "active") as the concentration of the catalyst increases, when the assumption is made that the undissociated molecule is active as well as the ions. These conclusions are in agreement with Rice's modification of the Marcellin equation, and with the theory that chemical reactivity is due to infra-red radiation.—J. P. O.

*Sugars; Purity of the molasses adhering to raw (beet)* —. A. Herzfeld. *Z. Ver. deut. Zuckerind.*, 1915, 65, 1. *Chem.-Zeit.*, 1915, 39, Rep. 43.

EXPERIMENTS made on 58 samples of raw beet sugars which had been stored for some time, indicated that the purity of the adhering molasses varies irregularly between the extremes of 60° and 75°. No relationship could be detected between the crystal content, the rendement value, the dry substance, and the calcium content of the sugars. The refining value of a raw sugar appears to depend largely upon its appearance, its purity,



the colour of its grain, and the nature of its solution in water.—J. P. O.

*Sucrose: The direct and the inverted polarisation of pure —.* H. S. Walker. Hawaiian Chem. Assoc., Oct. 22, 1911. J. Ind. Eng. Chem., 1915, 7, 216—217.

Sucrose was prepared from a high-grade sugar of such a degree of purity that it contained only 0.02%  $H_2O$ , 0.004% ash, and less than 0.016% reducing sugars (using Ost's solution). The direct polarisation of this sugar (26 grms. dissolved in 100 true c.c. of solution) was 99.80 at 22° C. By adding 0.06 as temperature correction and 0.02 for reducing sugars and ash, the polarisation of 26 grms. of pure sucrose dissolved in 100 true c.c. of solution is given as 99.88 at 20° C. By the double polarisation (Clerget-Herzfeld) method the percentage of sucrose, corrected for reducing sugars and ash, was 100.07. In a similar manner a sample of pure sucrose from the U.S. Bureau of Standards ( $H_2O$ , 0.0025%; ash, 0.002%; invert sugar, less than 0.003%; theoretical direct polarisation, more than 99.99) gave a direct polarisation of 99.90 and a sucrose content of 100.09 by the Clerget-Herzfeld method. These results indicate that to obtain a reading of 100% for pure sucrose with the present sugar scale, the Clerget factor should be increased from 112.66 to 112.78, whilst to give the same figure as the direct polarisation irrespective of the scale used, it should be increased to 112.92.—A. S.

*Starch: Modification of — by gaseous hydrochloric acid.* F. C. Frary and A. C. Dennis. J. Ind. Eng. Chem., 1915, 7, 214—216.

LACNDRY starch was powdered until 70% passed a 100-mesh screen, and the fine powder (12.7%  $H_2O$  by drying at 165° C.) was treated in a revolving mixer with hydrogen chloride gas dried by sulphuric acid: 20 grms. of starch was used in each experiment, and the amount of acid absorbed was determined by titrating a 1 gm. sample with N 10 alkali in presence of methyl orange. The results indicate that the method is suitable for obtaining dextrin of good adhesive power, but not for producing soluble starch, because at low temperatures the amount of acid required is excessive, and at higher temperatures it is difficult to prevent rapid conversion to dextrin. Dextrin of good adhesive power and colour was obtained in 5 mins. at 80—100° C. with 1.12% of acid, in 20 mins. at 90° C. with 1.81%, in 30 mins. at 80° C. with 2.06%, in 15 mins. at 50° or 20 mins. at 60° C. with 3.88%, and in 30 mins. at 100° C. with 0.33% of acid.—A. S.

*Manufacture of spirit and pressed yeast from raw sugar.* Reinke. See XVIII.

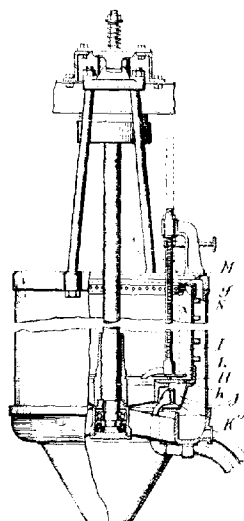
*Dextrose preparations from various carbohydrates.* Panzer. See XVIII.

#### PATENTS.

*Sugar solutions: Method of clarifying —.* Centrifugal separator. E. W. Kopke, Honolulu, Hawaii, Assignor to Kopke Clarifier Co., Ltd. U.S. Pats. (A) 1,119,174 and (B) 1,119,175, Dec. 1, 1914. Date of appl., Sept. 28, 1911.

(A.) IN the continuous clarification of liquids, e.g., sugar juices, by centrifugal stratification, in order that the crude liquid may enter the stratifying chamber with the proper angular velocity, without emulsification and without disturbing the established strata, it is first introduced in the form of a thin ribbon at an acute angle upon a previously introduced body of the same liquid contained in a smooth, unobstructed, annular antechamber of the rotating vessel, so that each

stratum of the introduced liquid is accelerated by the preceding stratum in an outward direction. The outermost layer of the liquid in the antechamber, having attained the full velocity of the apparatus, is admitted as a thin, hollow cylinder, moving axially, beneath the surface of the liquid contained in the superposed stratifying chamber, in which separation of the suspended solid matters takes place, and a selected stratum of the separated liquid is discharged from the stratifying chamber by cylindrical overflow at the end opposite to that at which the liquid was introduced. (B.) In the figure, I is the imperforate, unobstructed stratifying



chamber having a relatively shallow radial depth indicated by the dotted line *x*. *J* is the antechamber having an inclined outer wall *f*, and a number of apertures, *h*, in the outer portion of the partition, *I*, separating the two chambers. The crude liquid is introduced through the pipe, *K*, and ascends through the apertures, *h*, being then distributed by the baffle plate, *L*, so as to enter the chamber, *I*, as a continuous tubular body of liquid at a point between the outer wall and the level indicated by the line, *x*. At the upper end of the stratifying chamber, the in-turned flange, *g*, is provided with a channel, *M*, the outer wall of which is perforated with apertures, into which nozzles, *N*, of variable length are inserted to collect the liquid for discharge from any desired depth of the stratified body.—J. F. B.

*Dextrins: Process for obtaining crystallised —.* H. Pringsheim. Ger. Pat. 279,256, Sept. 23, 1913.

CRYSTALLISED dextrins are produced by the action of *Bacillus macerans* on starch and are isolated by precipitation with light petroleum spirit. (See also this J., 1911, 439; 1912, 1001; 1913, 985.)—A. S.

*Centrifugal separators.* U.S. Pats. 1,119,173 and 1,119,176. See I.

*Process for rapidly preserving in sugar (crystallising) fresh fruit.* Eng. Pat. 3867. See XIX.

#### XVIII. FERMENTATION INDUSTRIES.

*Hops: Investigations on —.* F. Aron, J. Schmidt. Comptes rend. Trav. Lab. Carlsberg, 1915, 11, 149—163. (See also this J., 1915, 13.)

OWING to the difficulty of preventing fertilisation by foreign pollen in hop gardens, even in Germany

and Austria where the male plants are eliminated as far as possible, probably all the older commercial varieties of hops are more or less mixed types. Investigations on hops for scientific or industrial purposes should be based on the study of clones (a clone is a group of plants derived originally from one individual by cuttings, all shoots and seedlings being eliminated). In 1911, individuals of several foreign varieties (Saaz hops from Bohemia, and two American types with very pronounced odour reminiscent of turpentine) were employed for the propagation of clones in the garden of the Carlsberg Laboratory. The clone-plants obtained up to the present have shown no deviation from the original types, as regards either aroma or appearance of the hops, so that the aroma of hops does not appear to be so "volatile" a character or so entirely due to local conditions as has been generally believed. When the two American types were crossed with Danish male plants, the characteristic aroma was transmitted to between 50 and 75% of the offspring; this result confirms some experiments made by E. S. Salmon at the Wye Agricultural College, Kent ("Notes on hops, 1912-1914").—J. H. L.

*Wort; Preservation of*.—F. Schönfeld, Woch. Brau., 1914, **31**, 354. J. Inst. Brewing, 1915, **21**, 201.

To meet the fluctuating demand of an uncertain trade in beers for quick consumption, it may be economical to make large brews and to preserve the wort in a sterile condition for fermentation as and when required. Suitable storage is provided by cylindrical metal tanks, after the pattern of those used for the cultivation of pure yeast by the Stockhausen-Coblitz method, holding 1-10 hectolitres (22-220 galls.) of wort. These are filled with the hot wort and closed with a cover having a rubber washer and held down by a weak spring; as the wort cools the cover is drawn down and closes the tank gas-tight. To prevent the collapse of the tank under the partial vacuum, the bottom, which is constructed of relatively thin metal, is made convex and is drawn inwards as the contents of the tank contract.—J. F. B.

*Wort and beer; Free and combined organic acids in*.—W. Windisch and K. ten Doornkaat Koolman, Woch. Brau., 1914, **31**, 225-228, 235-237, 252-255, 275-282, 295-296, 303-308, 311-316. J. Inst. Brewing, 1915, **21**, 205-208.

The separation of the organic acids from other substances which affect indicators, e.g. phosphates, proteins, etc., is effected by continuous extraction for 48 hours with ether in a modified form of the Parthel-Rose apparatus, before and after acidification of the beer with a mineral acid. The ethereal extracts are titrated with barium hydroxide in presence of rosolic acid and the volatile acids then separated by distillation with steam under reduced pressure. Worts contain considerable quantities of combined organic acids but very little in the free state; after fermentation the quantities of both are large. The composition of the wort as regards inorganic salts has an important influence on the production of acids by the yeast; hence the effect of the brewing water. A high proportion of carbonates in the water stimulates the yeast to produce acids; a wort prepared with such a water showed an increase of organic acids from 3.1 to 6.3% during primary fermentation and a further increase to 7.9% during storage of the beer. Wort from the same malt with the same water de-carbonated by treatment with sulphuric acid contained an initial 6% of total organic acids, which increased to 8.6% during fermentation and then fell to 8.4% during storage. Wort made with de-carbonated water, under conditions specially favourable to proteolysis, contained initially

7.7%, rising to 12% during fermentation but falling to 8% during storage. Hence it would appear that the yeast tends to produce a quantity of acid which ultimately approximates to a definite value for a given wort. The formation of free organic acids is subject to the same conditions; these affect the flavour both directly and after esterification. When brewing water rich in carbonates is employed the free organic acids, like the total organic acids, increase during storage; long storage of such beers is therefore likely to improve their flavour, and it might be advisable to rack them at an earlier stage than beers made with waters only moderately rich in carbonates and sulphates. As regards lactic acid, worts made with waters rich in carbonates contain least, but after fermentation the beers may contain as much or more than those made with de-carbonated waters. In general an increase in the acidity of wort or beer is best detected by titration in presence of litmus, as the results are only affected by the hydrogen ions present. Worts prepared with a water rich in carbonates are less acid to litmus and less alkaline to methyl orange than those made with the same water after de-carbonation either by boiling or neutralisation. Of the volatile acids of beer, the greater part is in the free state, whereas the greater part of the non-volatile acids is combined with bases. Of the total lactic acid about one-third is free. —J. F. B.

*Yeasts; Assimilation of nitrogenous matters by top-fermentation*.—F. Schönfeld and R. Klot, Wochensh. Brau., 1914, **31**, 345-346. J. Inst. Brewing, 1915, **21**, 201-205.

In bottom-fermentation beer worts, 45-65% of the total nitrogen is assimilable by yeast but only about one-third of this is actually consumed in brewery fermentations. In general, yeasts which produce high attenuations assimilate more nitrogen than low-attenuating varieties, but with top-fermentation yeasts a higher proportion of the assimilable nitrogen is taken up by the yeast even when the attenuation is low (*Doppelbier*, *Karamelbier*). In the case of Berlin *Wassbier*, with an apparent attenuation of 75, the yeast absorbs as much as two-thirds of the total assimilable nitrogen of the wort. The difference between the behaviour of top- and bottom-fermentation yeasts in this respect is probably partly due to the higher temperature at which top-fermentation is conducted and partly also to the racial characters of the yeasts.—J. F. B.

*Alcoholic fermentation; Pyruvic acid as catalyst for*.—M. Oppenheimer, Z. physiol. Chem., 1914, **93**, 233-261.

Sodium pyruvate was found to accelerate the fermentation of dextrose by yeast maceration juice in a remarkable degree. In one experiment, addition of 0.1% to juice containing 1% of dextrose increased the production of carbon dioxide nearly sevenfold during the first hour, and about threefold during 24 hours, the total gas theoretically obtainable being produced within the latter period. Addition of only 0.01% of sodium pyruvate had practically the same effect, but the acceleration produced by higher concentrations, such as 1%, was much less. Various investigators have stated that free pyruvic acid is not readily fermented (cp. Neuberg and others, this J., 1911, 379, 1179, 1180; 1913, 620, 803), but the author found that 1% solutions in yeast juice were fermented as continuously as, and more rapidly than, 1% solutions of dextrose, and further that the free acid accelerated the fermentation of dextrose, though not to the same extent as its salts. At concentrations of 0.1 or 0.01% it had little effect, but at 1% the acceleration was

considerable. In view of these facts the results of fermentation experiments with pyruvic acid in presence of carbohydrates must be interpreted with caution; effects attributed to the action of carboxylase may have been due to some extent to stimulation of fermentation of carbohydrates. The fermentation of dextrose by yeast juice was found to be somewhat accelerated by very low concentrations (about 0.0005%) of acetaldehyde, which is a product of the decomposition of pyruvic acid by carboxylase (cp. v. Lebedeff and Griaiznoff, this J., 1913, 1195; Kostlytschew and Hübner, this J., 1913, 741). Sodium pyruvate considerably accelerated the fermentation of dihydroxyacetone by yeast juice, but not that of glyceraldehyde. In view of the general catalytic influence of pyruvic acid on fermentation, the author finds evidence for the fermentability of lactic acid (see this J., 1914, 156) in the observation that the production of carbon dioxide from a solution of these two acids in yeast juice was greater than from a control solution of pyruvic acid alone.—J. H. L.

*Beers containing iron.* F. Schönfeld. *Wochenschr. Brau.*, 1914, 31, 321–322. *J. Inst. Brewing.*, 1915, 21, 213–215.

BEERS containing iron and possessing medicinal or dietetic qualities are manufactured in Germany; the percentage of iron ranges between 0.0002 and 0.011, without rendering the beer unpalatable. The introduction of iron may be effected by leaving the beer in contact with chemically pure iron, or more rapidly by the addition of insoluble compounds of iron, such as the hydroxide, the acids present in the beer exerting a solvent action. The same end is more readily attained by adding to the beer certain soluble pharmacological preparations, e.g. *Ferrum albuminaturn*, *F. peptonatum dial.*, *F. oxydatum sacch.*, *F. lacticum*, *F. citricum oxydul.*, *F. glycerino-phosphoricum*. The chief difficulty is due to the instability of the mixtures on storage, part of the iron being deposited as a "haze" or even as a sediment, owing to secondary reactions with the phosphates, organic acids, and tannin constituents of the beer. *Ferrum lacticum* is one of the most stable preparations, but its use is restricted on account of its marked influence on the flavour. There are two commercial preparations of sugar containing iron (*Eisenzucker*), one of which is alkaline and relatively stable; this remains soluble in beer for a considerable time, but eventually a precipitate is formed. The most suitable types of beer are the dark varieties which have been heavily primed with sugar. The sugars and caramels disguise the flavour of the iron and, as these beers contain less phosphoric acid and tannins than other types, there is less likelihood of precipitation. A high temperature of storage accelerates the secondary reactions which lead to precipitation of the iron.—J. F. B.

*Wines; Acidity of* ——. C. Mensio and E. Garino. *Annali R. Accad. Agric. Torino*, 1914, 56, 138. *Annali Chim. Appl.*, 1915, 3, 148–149.

THE values for the acidity of wine as determined by the effect on the inversion of sucrose at 76° C. and on the hydrolysis of ethyl diazoacetate are not always equal. As determined by the effect on the inversion of sucrose, the acidity of ordinary table wines was equal to that of N/1000 HCl, the acidity of dry, white wines was equal to that of N/1700 HCl, and the acidity of bouquet wines was equal to that of N/3000 HCl. The addition of 150–300 grms. of calcium sulphate per hectolitre produced a great increase in the acidity, whilst a similar addition of dicalcium phosphate had no effect. The increase of acidity produced by addition of phosphoric acid was less than that

caused by addition of sulphuric acid but about equal to that produced by addition of calcium sulphate.—A. S.

*Vinegar eels; Destruction of* ——. J. F. Sacher. *Chem.-Zeit.*, 1914, 38, 1186.

THE author has stated recently that vinegar eels are killed within a few days when 0.1% of hydrochloric acid is present in the vinegar in the free state (see this J., 1915, 193), whilst Henneberg found (*Biologie des Essigaales*, 1899) that the eels survived in vinegar to which 0.2% of hydrochloric acid was added. In explanation of this apparent difference it is pointed out that the greater part of the acid added would combine with the acetates, particularly calcium acetate, in the vinegar and but a small quantity, if any, of the acid would remain in the free state. Henneberg himself found that a 0.1% solution of hydrochloric acid in distilled water was fatal to the eels, whereas the addition of 0.1% of the acid to a vinegar containing 6.5% of acetic acid was without effect. It is evident that the eels are not destroyed by the gastric juice.—W. P. S.

*Spirit and pressed yeast; Manufacture of* ——. *from raw sugar.* O. Reinke. *Chem.-Zeit.*, 1915, 39, 149.

THE Prussian government has permitted the use of raw sugar denatured with 2% of lampblack for distillery purposes, with a reduction of the sugar tax to M.2 per 100 kilos. In employing raw beet sugar the addition of the sugar must be regulated in accordance with the quantities of nitrogen and phosphoric acid contributed by the other materials, such as cereals, yeast extract, etc.; the sugar must be sterilised by heat and its alkalinity corrected either by an increased acidity of the preliminary malt and rye mash or by the addition of lactic or mineral acid. If the sugar already has an acid reaction, the addition of 0.01% of sulphuric acid to the wash will be sufficient; the total acidity should be 0.2%, equivalent to 0.09% of lactic acid. Pure sucrose yields in practice 49.8% of alcohol, equal to 0.6274 litre per kilo. Raw beet sugar contains 90–96% of sucrose and 0.9–2.8% of ash; a raw sugar containing 92% of sucrose would yield 57.7 litres of alcohol per 100 kilos, if the wash is made up in the form of a 20% solution of sugar, with additions of malt-combs, malt, barley grist, or of large quantities of brewery yeast. In the latter case, 20 kilos. per 1000 litres is employed, of which 18 kilos. is pressed and submitted to plasmolysis at 68° C. for 2 hours, whereby soluble phosphates and nitrogenous matters are formed and the yeast is killed. With smaller additions of sugar, the thin washes are made up to a total concentration of 20%; the same holds good for yeast cultivation either by the old Vienna process or the aeration process.—J. F. B.

*Yeast; Measurement of the fermentative action of* ——. *by means of the liquid interferometer.* O. Wolff. *Chem.-Zeit.*, 1915, 39, 197–198. (See also this J., 1915, 371.)

THE interferometer was applied to the measurement of the rates of fermentation produced by different yeasts in 10% sucrose solutions. In standardising the instrument, a reading of 1847 was obtained when one 0.5 cm. cell was filled with a 10% solution of sucrose (by weight) and the other with a 10% solution of alcohol (by volume), the reading with both cells filled with the same solution being zero. The intermediate readings observed when mixtures of the two solutions in various proportions were used in the second cell, were strictly proportional to the alcohol-content of the mixtures. The experiments with yeast were carried

out as follows:—10 c.c. of a 5% suspension of yeast was added to 100 c.c. of 10% sucrose solution. Half of the liquid was at once heated to 60° C. to kill the yeast, and then centrifuged, and the clear liquid was employed in the first cell (1 cm.). The other half was maintained at 28.5° C. and portions were withdrawn at intervals of 1 hour, heated rapidly and centrifuged, and the clear liquid introduced into the second cell. The readings observed, plotted against the duration of fermentation, gave in all cases a fair approximation to a straight line graph, though in some cases there were irregularities during the first three hours. The curves for the seven yeasts investigated showed marked differences in their inclination to the axes, and the method thus affords a means of comparing the rates of fermentation produced by different yeasts.

—J. H. L.

*Alcoholic liquors; Determination of the iodine value of— by Hübl's method. Iodine value of essential oils.* R. Marcille. Ann. Chim. Analyt., 1913, 20, 52–57.

EXPOSURE to light and the alcoholic strength of the solution have a considerable influence on the results obtained in the determination of the iodine value of alcoholic liquors containing essential oils. In the following table the figures express grms. of iodine per grm. of essential oil, and grms. of iodine per litre in the case of absinthe:—

	In the dark.	In diffused light.	In bright light.
Anised oil dissolved in 95% alcohol	1.35	1.54	1.62
do. do. 50% do.	1.27	1.80	1.57
Turpentine oil do. 95% do.	3.19	—	2.67
do. do. 50% do.	3.36	3.18	1.78
Absinthe liqueur	2.7	3.7	3.1

The concentration of the essential oil solution and the temperature during the time of contact of the solution with the Hübl reagent have also some influence on the results. Therefore, in determining the quantity of essential oil in an alcoholic solution by means of the Hübl method, a control experiment should be made at the same time and under the same conditions, using in this control or standard, a solution of equal alcoholic strength and containing approximately the quantity of the oil present in the solution under examination.—W.P.S.

*Diastatically active substance from lactose: Production of a —. XII.* T. Panzer. Z. physiol. Chem., 1914, 93, 316–336. (See also this J., 1913, 41, 441, 547, 620, 669, 707, 708, 837, 920.)

Dry powdered lactose exposed to a current of dry hydrogen chloride and afterwards to ammonia, by the method previously applied to invertase and diastase, acquired a feeble capacity for saccharifying starch. In two cases the product was sufficiently active to yield saccharification tests showing only a red coloration with iodine; but such products could not be prepared at will, and in most cases the only evidence of diastatic power was a slight increase in the reducing power of the test liquids. By boiling solutions of the treated lactose the activity was destroyed. The treatment with ammonia was indispensable for the preparation of active products, for lactose which had been simply exposed to hydrochloric acid and then stored *in vacuo* over sulphuric acid and soda-lime remained inactive. The effect of the latter treatment in conferring slight activity on diastase previously made inactive by heat (see this J., 1913, 837, 920) may be due to the presence of nitrogenous matters which renders exposure to ammonia unnecessary.—J. H. L.

*Diastase preparations from various carbohydrates.*

T. Panzer. Z. physiol. Chem., 1915, 93, 339–354.

PRODUCTS similar to that obtained from lactose, (see preceding abstract) are also obtained when starch, dextrin, gum arabic, sucrose, maltose, dextrose, and galactose are treated successively with hydrochloric acid gas and ammonia gas. In the case of sucrose and dextrose, the diastatic product is obtained only when the sugar is subjected to the successive action of ammonia, hydrochloric acid, and ammonia. Lævulose was the only sugar which did not give an active product.

—W. P. S.

*Apple cider; Manufacture of concentrated — in America.* J. Roy. Soc. Arts., 1915, 63, 461.

THE U.S. Department of Agriculture, through its Fruit and Vegetable Utilisation Laboratory, is about to make a commercial test of a new method of concentrating apple cider, in which the cider is frozen and the ice crushed and submitted to centrifugal action, whereby the concentrated juice is expelled, leaving about 80% of the water as ice.

*Prizes for methods of denaturing and utilising spirit in Russia.*

THE Russian Ministry of Finance offers prizes of 30,000, 15,000, and 5,000 roubles to international competition, for new denaturing agents for improving the existing methods of denaturing. The agents must convert the spirit into a liquid unfit for direct use as a beverage, and should be of such nature that they do not spread a suffocating odour which renders the use of the spirit inconvenient or injurious. They should not leave a residue on combustion, nor contain elements which would damage the apparatus in which the spirit is burning. The separation of the denaturants from the spirit by means of simple methods (by water, salting, filtering through charcoal, simple distillation, etc.) must be impracticable. The primary substances, from which the denaturing agents are prepared, must be obtainable in Russia in suitable quantities.

Prizes of 60,000, 30,000, and 10,000 roubles are also offered for a new method of adapting spirit to the preparation of a product different from the spirit used in its preparation (e.g., vinegar, ether, chloroform, etc.).

Prizes of 50,000, 20,000, and 5,000 roubles are offered for a new method to apply spirit for the preparation of a product in which the spirit or its derivatives (sulphuric ether, etc.) form one of the constituent parts of the product or serve as solvent (e.g., pharmaceutical and perfumery preparations).

Prizes of 30,000, 15,000, and 5,000 roubles are offered for methods for applying spirit in an industry in which the spirit or its derivatives (sulphuric ether, etc.) should serve either as a transitory intermediate solvent or an extracting or precipitating substance; as, for instance, in the preparation of smokeless powder or artificial silk.

Four prizes respectively of 75,000, 50,000, 30,000, and 20,000 roubles for an invention or improvement relating to apparatus for utilizing spirit in internal combustion engines, and similar prizes for apparatus for utilizing spirit or its derivatives as fuel.

Four prizes respectively of 50,000, 30,000, 15,000, and 5,000 roubles are offered in connection with apparatus for applying spirit to lighting purposes.

Competitors must present their declarations not later than January 1st, 1916, in Russian or French languages, to the Department of Unassessed Taxes and Spirit Monopoly (Glavnoe Oupravlenie Neokladnich Sborow i Casennoi Prodagy Pitei, Petrograd). Further particulars may be obtained from Messrs. E. P. Alexander and Son, 306, High Holborn, W.C.

## PATENTS.

*Beer, stout, and other liquids: Machines for carbonating*—, P. Wilkinson, Manchester. Eng. Pat. 12,109, May 16, 1914.

THE supply of liquid to the carbonating vessel is controlled by a by-pass pipe fitted to the bottom of the vessel and connecting it with the suction-side of the pump. The orifice of this pipe inside the vessel is closed by a valve controlled by a float which opens the by-pass when the liquid rises above the desired level.—J. F. B.

*Amylaceous materials: Process for the liquefaction, saccharification, and fermentation of*—, A. Boidin and J. Effront. First Addition, dated July 11, 1913, to Fr. Pat. 461,853, Nov. 7, 1912 (this J., 1914, 213).

HOT water is circulated in the vessel in which the grain is steeped and through an external pipe provided with injectors for steam and compressed air to maintain the temperature and circulation. When sufficient water has been absorbed, depending on the hardness of the corns, the grain is discharged through the same pipe into a screw-conveyor working in a perforated trough. The excess of water drains back into the steeping tank, while the grain is delivered through crushing rollers into the starch-converting vessel.—J. F. B.

*Amylaceous materials: Saccharification and fermentation of*—, A. C. Molhant. Fr. Pat. 471,775, July 18, 1913.

STARCHY materials are liquefied by digestion with boric acid or its compounds, the quantity of malt required for their ultimate saccharification being thereby reduced. Fermentation is effected by special yeasts acclimatised to boric acid.—J. F. B.

*Alcoholic fermentation: Product intended to promote and control - - - and process of making same*, V. A. Sebastian. Fr. Pat. 471,784, July 19, 1913.

SULPHITED citrophosphate of ammonium is added to the must in the proportion of about 40 grms. per 130 kilos, of grapes or per 100 litres of wine. The components of the sulphited citrophosphate may be combined in various ways, e.g. by passing sulphur dioxide into a solution containing citric acid, phosphoric acid, and ammonia, suitable proportions being equivalent to 280 grms. of triammonium phosphate and 260 of sulphur dioxide.—J. F. B.

*Yeast: Manufacture of - - - from worts containing little or no sugar*, Verein der Spiritusfabrikanten in Deutschland. Fr. Pat. 472,073, May 6, 1914. Under Int. Conv., May 6, 1913.

YEAST is cultivated by the "aeration" process, without appreciable production of alcohol, by growth in worts previously deprived of sugar by bacterial acidification. The yeast derives its carbon nutrition from the organic acids, which may be neutralised during the process of acidification by the addition of alkalis, being afterwards liberated by means of mineral acids. If sugar be present during the cultivation of the yeast, the proportion of free organic acids should be at least 10% of the total extract. Spent wash from distilleries may be used for making up the wort, and the process may be combined with that of the manufacture of starch by the acidification process, the yeast being cultivated in the clear liquor separated from the starch or from the mixture of liquor and ungelatinised starch. In certain cases the yeast and lactic acid bacilli may be cultivated simultaneously.—J. F. B.

*Enzymes and lozins: Method and apparatus for the manufacture of - - - by oxidising ferments*, A. Boidin and J. Effront. Fr. Pat. 471,546, July 11, 1913.

ENZYME solutions of high diastatic power are prepared by cultivating micro-organisms in worts very rich in nitrogenous constituents, particularly in extracts of soy beans or the oil-cake derived therefrom. The apparatus is constructed of aluminium or enamelled metal and consists of a digester for preparing the extract, a closed cultivation vessel which can be charged under sterile conditions from the digester, and means for providing a free circulation of sterilised air from above downwards. The micro-organisms are cultivated in the form of films, the vessel being filled with a number of superposed shallow trays to which a slight reciprocating motion may be imparted at intervals by means of a central shaft and external gearing to assist diffusion without submerging the film. A strong superficial aeration is provided in the early stages, being gradually decreased as the growth accumulates; when the culture is ready the trays may be emptied by centrifugal force and refilled with further quantities of sterilised wort.—J. F. B.

*Amylaceous substances: Process and apparatus for the liquefaction, saccharification, and fermentation of*—, A. Boidin, Seclin, France, and J. Effront, Brussels. Eng. Pat. 23,738, Oct. 20, 1913.

SEE Fr. Pat. 461,853 of 1912; this J., 1914, 213.

*Maturing or ageing wines, spirits, or other potable liquors: Process for artificially*—, V. Henri, A. Helbronner, and M. von Recklinghausen, Paris, Assignors to The R.U.V. Co., New York. U.S. Pat. 1,130,400, March 2, 1915. Date of appl., May 31, 1910.

SEE Fr. Pat. 493,674 of 1909; this J., 1910, 104.

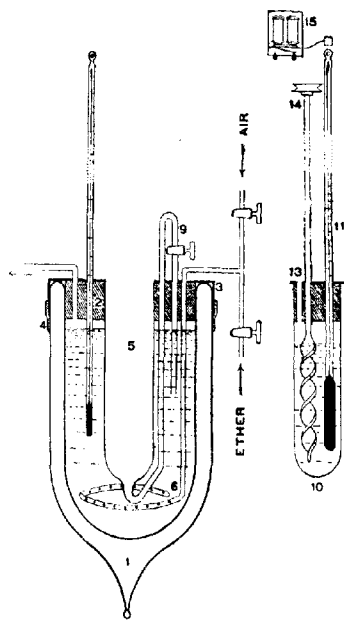
## XIXa.—FOODS.

*Milk: The freezing point of - - - considered in its relation to the detection of added water*, G. W. Monier-Williams. Report to the Local Gov. Board, 1914. Food Report No. 22, 1-32.

THE first part of the Report deals with the factors influencing the correct determination of the freezing point of a solution, e.g., sources of error inherent in a mercury thermometer, mechanical production of heat by the stirrer, too low a temperature of the freezing bath, increase in the concentration of the solution owing to separation of ice (supercooling), etc. The accuracy of the thermometer scale is best controlled by a comparison of the freezing points of sucrose solutions of known strength with the very accurate values given by Raoult (*Z. physik. Chem.*, 1898, 27, 617); a table showing these values is given in the Report. The errors introduced by the stirrer and by having the temperature of the bath too low, may be eliminated by so regulating the temperature that the freezing point of the solution coincides with the so-called "temperature of convergence," i.e., the point at which the solution is in exact heat equilibrium with its surroundings. The convergence temperature varies with the apparatus and must be determined by experiment; in the apparatus described below it was found to be 0.24° C. above the bath temperature. The error due to increase in concentration owing to the formation of ice may be very large and appears to have been overlooked by most investigators. If a solution is cooled below its freezing point and a minute fragment of ice is introduced, formation

of ice occurs in the liquid and the temperature rises immediately to a point which approximates the true freezing point. Owing to the separation of the ice, however, the observed freezing point will be that of a solution more concentrated than the original solution. Raoult has shown that the effect of supercooling may be expressed by the equation:  $K = \frac{C' - C}{CS}$ , where  $C'$  = the observed value,  $C$  = the true depression,  $S$  = degrees of supercooling, and  $K$  = a constant. The latter is found by determining the freezing point for different degrees of supercooling; if the values found are plotted as ordinates and the degrees of supercooling as abscissæ, an approximately straight line is obtained from which the true freezing point for supercooling *nil* may be found.  $K$  is then calculated from the above formula. For sucrose solutions  $K = 0.015$  and for milk  $K = 0.017$ .

The apparatus used in the determinations is shown in the illustration. A Dewar vacuum vessel, 1, of 10 cm. internal diameter and 16 cm. internal



depth, was closed with a cork disc, 2, about 1 inch thick, glued to a metal plate and ring, 3, and the cover thus formed could be made air-tight by a rubber ring, 4. Through the middle of the cork disc passed a glass tube, 5, of 3.8 cm. internal diameter, the joint with the metal plate being made air-tight with glue-cement. The cork disc also carried a copper inlet tube for ether and air, an outlet tube, a thermometer graduated to 0.01°C., and a siphon, 9, connected with the lower end of the tube, 5, and so designed that ether could be admitted or withdrawn from the Dewar vessel. The freezing tube, 10, was a thin glass test-tube, 3.5 cm. internal diameter; it was closed by a cork, 1 inch thick, carrying the thermometer, 11, a spiral glass stirrer, and a small opening, 13, provided with a stopper. It also carried another thermometer, not shown in the figure, graduated to 0.1°C., to indicate the degree of supercooling. The freezing point was determined in the following manner:—Ether, dried over calcium chloride, was

drawn into the Dewar vessel until the latter was full. About 60 c.c. of liquid, of which the freezing point was to be determined, was introduced into the tube, 10, which was then closed with the cork and introduced into the freezing tube, 5. Ether was allowed to flow from the Dewar vessel through the siphon, 9, into the space between the tubes, and the stirrer was connected with the rotating spindle, 14, driven by an electric motor. The supply of ether was now shut off, and a rapid current of air drawn through the apparatus. As the ether evaporated it was replenished by shutting off the air supply and opening the tap connecting with the ether supply. In this way the temperature of the bath could be lowered to  $-4^{\circ}\text{C}$ . in 15–20 minutes. The ether in the space between the tubes, 5, and 10, served as a heat conducting medium, and the temperature of the solution was lowered far more rapidly than when the space contained air. The stirrer was rotated at a constant speed of about 1300 revolutions per minute. When the solution had reached the desired degree of supercooling, i.e. about  $0.5^{\circ}\text{C}$ . below the expected freezing point, the air supply was shut off, and the tap on the siphon tube, 9, opened. The ether in the space between the tubes, 5, and 10, was thus replaced by air. The tap on the siphon tube was now closed and ether at the ordinary temperature drawn into the Dewar vessel until the temperature of the bath had risen to a point about  $0.24^{\circ}\text{C}$ . below the expected freezing point. The degree of supercooling was noticed, and a minute fragment of ice introduced through the opening, 13. A small electric hammer, 15, was then set in motion (the succession of sharp taps given to the thermometer by this hammer prevented the "lag" or sticking of the mercury in the fine capillary), and the point to which the mercury of the thermometer, 11, rose, was observed through a telescope at a distance of a few feet, the temperature of the bath being kept constant by drawing ether or air through it as required. The thermometer, 11, had a total range of about  $1^{\circ}\text{C}$ ., divided into intervals of 0.005; each 0.005 division occupied a length of about 0.4 mm. The observed freezing point remained constant for an indefinite period, provided that the bath temperature and the speed of the stirrer did not alter. For practical purposes, the process may be simplified by dispensing with the determination of the zero point given by distilled water, and comparing the freezing point of the milk sample with that of a solution of 9.195 grms. of pure sucrose in 100 grms. of water; this solution freezes at exactly  $-0.5345^{\circ}\text{C}$ ., the average freezing point of normal milk. If the two determinations are carried out in precisely the same manner, the difference between the two results will indicate fairly accurately the true freezing point of the milk in question. The bath may be ice and salt and the temperature as low as  $-5^{\circ}\text{C}$ . The freezing point of milk is not appreciably affected by the removal of the fat, but the development of acidity to any great extent has a considerable influence. The increase of acidity, however, is very slow during the preliminary stages of souring and the taste and smell of the sample are very good guides as to whether or not the freezing point method is applicable; a sample has to smell and taste distinctly sour before the freezing point is depressed by as much as  $0.002^{\circ}\text{C}$ . Pasteurisation for 20 minutes at  $60^{\circ}\text{C}$ . raises the freezing point by about  $0.002^{\circ}\text{C}$ .

The average freezing point of 141 samples of genuine milk was found to be  $-0.5345^{\circ}\text{C}$ ., the values found ranging from  $-0.558^{\circ}\text{C}$ . to  $-0.514^{\circ}\text{C}$ .; these values have been subjected to all the necessary corrections and are probably accurate to about  $0.002^{\circ}\text{C}$ . The freezing point appears to be the most constant of any of the

properties exhibited by milk. It is unaffected by the addition of separated milk to genuine milk, but it is raised by the addition of water. The method may, in certain cases, be applied with advantage, as a confirmatory test, to the detection of added water and to the approximate determination of the amount present, but owing to the experimental difficulties involved in obtaining reliable results, it does not appear to be capable of general application for purposes of milk control.—W. P. S.

*Milk; Coagulation of—, and the solubility of the curd in salt solution.* Orla-Jensen, B. Meyer, and A. D. Orla-Jensen. *Z. physiol. Chem.*, 1914, 93, 283—306.

THE investigation relates to coagulation by calcium chloride, rennet, and acids. Mono-, di-, and tri-calcium and sodium caseinates are all salted out from aqueous solution by calcium chloride in the cold, the mono-salts most readily and the tri-salts least readily. Similar coagulation of the casein in milk by calcium chloride takes place only on warming. It is probable that the first step is a disturbance of the equilibrium between the salts of the milk, resulting in increased acidity and precipitation of lime as phosphate and probably as citrate, after which the dicalcium caseinate is coagulated by the calcium chloride as in pure aqueous solutions. A 3% solution of dicalcium caseinate containing 0.08% of calcium chloride is curdled by rennet in the same way as cow's milk. Solutions of mono- and tri-calcium caseinates may also be coagulated by rennet if they contain at least half as much calcium chloride as would by itself produce coagulation. To coagulate solutions of sodium caseinates with rennet, a slight excess of calcium chloride over that necessary to convert the casein into calcium salts, must be added. The coagulation of milk or solutions of pure caseinates with rennet, which, according to Hammarsten, is a proteolytic transformation, is not accompanied by any increase in the quantity of free amino-groups as measured by titration with acid after treatment with formaldehyde (see Sørensen, this J., 1908, 135). In the curdling of milk by acids at about 35° C., coagulation begins before all the caseinates have been converted into free casein, but is only complete when sufficient acid has been added to extract completely the calcium from the casein. At 60°—80° C. smaller quantities of acid suffice for complete coagulation, but this is partly due to the dissolved calcium salts; for not only does the coagulating power of the latter increase with rise in temperature, but the added acid, by partially decomposing calcium caseinates, increases the concentration of the active calcium salts and converts dicalcium into monocalcium caseinate which is more readily coagulated by calcium ions. The calcium salts of casein and paracasein (the coagulable product of the action of rennet; see Hart and van Slyke, this J., 1905, 509) form clear liquids with sodium chloride solutions, being converted into sodium salts, but the presence of other calcium salts tends to inhibit this reaction, especially with the dicalcium compounds. Hence the dicalcium caseinate in milk is difficult to bring into solution with salt, unless sufficient acid is first added to convert it into monocalcium caseinate; and the same applies to the paracaseinates in milk curdled by rennet. By using larger amounts of acid than are necessary to extract the calcium completely from the casein (or paracasein), soluble acid-albumins are formed, which are less soluble in 5% sodium chloride solutions than the original proteins. With milk the maximum solubility of monocalcium caseinate or paracaseinate lies at a concentration of 5—10% of sodium chloride; at a concentration of 25%

monocalcium caseinate is salted out as completely as the dicalcium compound.—J. H. L.

*Condensed milk, evaporated milk, concentrated milk.* U.S. Dept. Agric., Food Inspection Decision 158.

THE Joint Committee on Definitions and Standards of the American Association of Dairy, Food, and Drug Officials, the Association of Official Agricultural Chemists, and the United States Department of Agriculture, on November 20th, 1914, adopted the following definition and standard for condensed milk, evaporated milk, concentrated milk:—

Condensed milk, evaporated milk, concentrated milk, is the product resulting from the evaporation of a considerable portion of the water from the whole, fresh, clean, lacteal secretion obtained by the complete milking of one or more healthy cows, properly fed and kept, excluding that obtained within fifteen days before and ten days after calving, and contains, all tolerances being allowed for, not less than 25.5% of total solids and not less than 7.8% of milk fat.

Food Inspection Decision No. 131 is revoked.

*Proteins; Well-characterised organic sulphur compound obtained from— by treatment with nitric acid.* C. T. Möerner. *Z. physiol. Chem.*, 1914, 93, 175—202.

It is known that the whole of the sulphur present in proteins cannot be oxidised to sulphuric acid by nitric acid, and the author attempted to ascertain the nature of the resistant compound or compounds formed under these conditions. Large quantities of serum albumin, egg albumin, casein, ovomucoid, haemoglobin, keratin (sheep's wool), and gelatin (gelatin) were oxidised by excess of nitric acid, and from the products in all cases methylsulphonic acid was isolated in the form of its barium salt,  $(CH_3SO_3)_2Ba + 14H_2O$ . The amounts obtained varied from 1.4 to 12.4 grms. (of barium salt) per kilo. of protein, and bore no relation to the quantities of cystin present. Moreover, under the conditions of oxidation employed, cystin does not produce methylsulphonic acid, so that all the proteins investigated must contain some other form of combined sulphur.—J. H. L.

*Fatty acids and other ether-soluble constituents of feeding stuffs; Determination of the total—.* J. B. Rath. *J. Ind. Eng. Chem.*, 1915, 7, 218—220.

ALCOHOLIC alkali is used to extract the fatty matter. 10 grms. of the sample, or 5 grms. if it is bulky or contains more than 4% of matter soluble in ether, is boiled with 50 c.c. of 2N alcoholic soda for 1 hour under a reflux condenser, the mixture is filtered through asbestos, the residue washed ten times with boiling redistilled alcohol, the solution evaporated to 10 c.c., transferred to a separating funnel with hot water, acidified with 10 c.c. of acetic acid, and extracted warm with five successive 50 c.c. portions of redistilled ether. The ether extract is treated as described previously (this J., 1915, 195) to determine the unsaponified matter. The aqueous soap solution obtained in this process is heated to expel dissolved ether, cooled, treated with 8 c.c. of glacial acetic acid, and extracted with 40 c.c. of petroleum spirit of b. pt. below 75° C.; the suspended matter which settles to the bottom is removed with the aqueous layer, and this is extracted three times more with petroleum spirit. The united petroleum spirit solutions are washed with two 50 c.c. portions of water, and the aqueous liquid extracted with petroleum spirit, the extract being washed twice with water and added to the main portion, which is then evaporated and the residue of fatty acids dried till of constant weight. The aqueous liquid from the extraction of

the fatty acids contains saponified matter other than fatty acids. It is treated with hydrochloric acid and extracted as described above, but using ether instead of petroleum spirit. The above method gives results for total fatty acids one-fifth higher in the case of concentrated feeding stuffs and more than twice as high in the case of hays and excrements from them than those obtained by extraction with ether. The ether extracts of concentrated feeding stuffs contain on the average 11% and the ether extracts of hays and excrements 68% of non-fatty substances.—A. S.

*Nitrogen and fat in short-staple cotton-seed.* Wells and Smith. See XII.

#### PATENTS.

*Fruit; Process for rapidly preserving in sugar (crystallising) all kinds of fresh*—. J. Anfossi, Aix, France. Eng. Pat. 3867, Feb. 14, 1914. Under Int. Conv., Feb. 21, 1913.

THE fruit is immersed in a solution of sucrose and "glucose" of 10° B. (sp. gr. 1.075) heated to 60°–70° C.; fresh quantities of the solution are added to compensate for evaporation until, at the end of 24 hours, the solution has become concentrated to 33° B. (sp. gr. 1.297); the fruit is then removed, drained, washed with hot water, and glazed with sugar in the usual way.—W. P. S.

*Bread; Manufacture of*—. W. A. Hobbs, Pittsburgh, Pa. Assignor to C. Adams, New Rochelle, N.Y. U.S. Pat. 1,131,698, March 16, 1915. Date of appl., April 30, 1914.

To obtain loaves of superior whiteness, a small quantity of calcium hypochlorite is added to the flour, the mixture is allowed to stand, and, after being made into dough, is treated with sufficient of a neutralising agent to remove the alkalinity of the hypochlorite.—J. H. J.

*Coffee; Process of manufacture from cereals of a substitute for colonial*—. A. Pietsch, Fr. Pat. 471,901, May 7, 1914. Under Int. Conv., Oct. 29, 1913.

A CEREAL, such as barley, is steeped in a solution of substances giving rise to the aroma and taste of coffee, namely, tannin, furfural, citric acid, sugar, infusion of hops, pyridine, etc.; caffeine is not used. The mixture is heated, and when the grains have absorbed most of the liquid, they are removed, roasted and ground. This powder is added to about ten times its weight of boiling water and the infusion strained. More tannin, sugar, and pyridine are added to it, and a fresh supply of barley. When this grain has absorbed the infusion, it is roasted and ground, and possesses the aroma of coffee.—J. H. J.

*Fruit and vegetable dust and process of making same.* H. Friedenthal, Berlin-Niolassee, Germany. U.S. Pat. 1,130,588, March 2, 1915. Date of appl., July 30, 1913.

SEE Eng. Pat. 17,723 of 1913; this J., 1914, 330.

#### XIXB.—WATER PURIFICATION; SANITATION.

*Chemotherapeutic preparations and other antiseptics; Effects of*—on bacteria. O. Schiemann and T. Ishiwara. Zeits. Hyg., 1914, 77, 49. Chem.-Zeit., 1915, 39, Rep. 37.

SALVARSAN has a very strong antiseptic action on the germs of anthrax, erysipelas, and glanders.

Ethylhydrocupreine is similarly potent against pneumococci; even in dilutions of 1:500,000—1:1,000,000 the inhibitive action is marked, although the germs are killed but slowly; towards other germs it is less powerful. The selective action is approximately the same in serum as in broth; it is more pronounced in activated serum than in unactivated, whilst the reverse is the case with mercuric chloride. The effect of phenol is diminished less than that of mercuric chloride by using a serum medium, and to about the same extent in both kinds of serum. Salvarsan is markedly less active in ox-serum than in rabbit-serum. The action of salvarsan, mercuric chloride, and phenol in broth cultures is reduced considerably by addition of lecithin or cholesterol.

—E. H. T.

*Saponin; Influence of*—upon disinfectants. K. Rotky. Zentralbl. Bakteriöl., 1914 (I), 73, 195. Chem.-Zeit., 1915, 39, Rep. 58.

By the addition of saponin the disinfecting action of carbolic acid, tar preparations such as lysol and odorite, formalin, etc. is increased; that of hydrochloric acid, potassium hydroxide, and mercuric oxycyanide is unaffected; and that of silver nitrate and corrosive sublimate is decreased.—J. R.

*Dental cements; Germicidal efficiency of*—. P. Poetschke. J. Ind. Eng. Chem., 1915, 7, 195–202.

AN investigation of the germicidal efficiency of so-called "copper cements" or "copper oxyphosphates," which are mixed for use with a concentrated solution of phosphoric acid to which aluminium hydroxide and sometimes iron and nickel salts have been added. The cements usually consist of copper salts and zinc oxide, with various filling materials and colouring matters. They differ widely in germicidal activity, which is best determined by mixing the cement, allowing it to set and harden, then grinding it, adding a known quantity of the powder to saliva at 37° C., and preparing cultures at different dilutions on nutrient agar-agar in the usual way. Cuprous and cupric oxides and zinc oxide were found to possess marked germicidal properties, and the bactericidal effect of zinc oxide was enhanced by addition of cuprous oxide or iodide or cupric phosphate.—A. S.

*Purification of tannery effluents.* Veitch. See XV.

*Risk of poisoning by volatilised mercuric chloride.* Moll. See IX.

#### PATENTS.

*Water and other liquids; Process and apparatus for determining the degree of impurity of*—. Z. Wegrzecki. Fr. Pat. 471,351, April 25, 1914.

A KNOWN volume of the water is treated with a precipitant, such as basic lead acetate or alum. The mixture filtered through a layer of paper or other white material, and the filter is dried and the stained surface compared with a series of standard stains produced by known amounts of impurity.—J. H. J.

*Liquids; Means for sterilisation, filtration, and similar treatment of*—. L. Linden, Brussels. Eng. Pat. 5512, March 4, 1914. Under Int. Conv., March 10, 1913.

THE liquid is passed successively through a settling tank, a horizontal filter, a chamber divided by a vertical partition over which the liquid flows, a second horizontal filter, and a second settling tank.



On leaving the upper part of the latter, the liquid is treated with a suitable reagent, and passes through two mixing tanks and thence through a series of vessels exactly similar to the first set. The direction of flow of the liquid through the whole apparatus may be reversed to cleanse the filters, etc., and the liquid in the chamber between the filters may be drawn off through a tap at the bottom, thus causing any liquid above the surface of the filters to pass downwards and aid in the cleansing operation.—W. P. S.

*Sterilisation, filtration, and similar treatment of liquids.* L. Linden, Brussels. Eng. Pat. 6273, March 12, 1914. Under Int. Conv., April 19, 1913. Addition to Eng. Pat. 5512 of 1914. (See preceding abstract.)

IN the treatment apparatus, each filter compartment has a settling compartment associated with it, and each pair is arranged in series. At the extremes of the series are reaction chambers. The liquid flows downwards through each filter and upwards through each settling compartment. Along the top of the compartments is a frame covered with filtering cloth impregnated with a cream made from chalk, alum, or other substance which will act as a filtering and sterilising agent. The filters are cleansed by reversal of flow, and conical spaces are provided below each pair of vertical compartments for the collection of the removed matters.—J. H. J.

*Sterilising liquids: Process of and apparatus for* — J. Mérie, Paris. Eng. Pat. 9495, April 16, 1914. Under Int. Conv., April 26, 1913.

IN apparatus where the liquid to be sterilised is passed through a heat-exchanger before it enters the steriliser, means are provided for filling the steriliser and the outlet passage of the heat-exchanger with water. The steriliser is then heated, and, when the water has been sterilised, the liquid to be treated is introduced under constant pressure, driving the water out of the apparatus. At the end of the operation, the apparatus is again filled with water in readiness for subsequent use.—W. P. S.

*Sterilising water: Process and apparatus for* — G. Ornstein. Fr. Pat. 471,627, Feb. 12, 1914. Under Int. Conv., Feb. 14, 1913.

GASEOUS chlorine, supplied from a cylinder of the liquefied gas, is passed into the bottom of a tower filled with contact material where it meets a current of the water to be sterilised trickling downwards: the proportions of chlorine and water can be adjusted by taps on the respective supply pipes. The solution obtained runs from the bottom of the tower into a main pipe of the supply to be treated. A pressure regulator may be placed on the pipe admitting the chlorine gas to the tower. Four types of apparatus are described and illustrated.—J. H. J.

*Carbon dioxide; Absorbent for* — in breathing apparatus for use in mine rescue work or like purposes. E. J. Bevan and R. H. Davis, London. Eng. Pat. 22,719, Nov. 18, 1914.

WOOD pulp is ground with caustic soda solution until a crumbly substance is produced, which is more efficient than caustic soda in lumps or sticks as an absorbent of carbon dioxide and has special advantages in breathing apparatus.—J. H. J.

*Furnace for burning detritus, night soil, and the like.* Stettiner Chamotte-Fabrik Akt.-Ges. vorm. Didier. Fr. Pat. 471,411, April 27, 1914.

THE furnace is of the grateless type in which combustion takes place in the lower portion of the

descending refuse. The combustion chamber is surrounded by a water jacket, and at the level of the bottom of the jacket air is introduced through several tuyères which are of the shape of a double cone and form a circle round the chamber. To remove the layer of burnt material, a clinker cutter worked by hydraulic pressure is introduced through an opening in the wall of the furnace and detaches the clinker; it is then withdrawn on to its platform, which moves along rails to the next furnace to be operated. The bottom of the furnace is closed by a plate when combustion is going on, but when the cutter is to be operated, the plate is drawn out and its place taken by a cylinder, through which the clinker detached by the cutter falls and is guided on to a travelling band below.—J. H. J.

*Antiseptics, disinfectants, and germicides (from peat tar): Manufacture of* — G. T. Morgan, Dublin, and G. E. Scharif, Bray, Ireland. Eng. Pat. 19,253, Aug. 31, 1914.

PEAT tar is dried at 100° C. and distilled until a sample of the distillate solidifies on cooling. The distillate is extracted with a 10–15% solution of caustic soda, the extract is separated and neutralised with mineral acid, and the acidic oils which separate are fractionally distilled, the fractionation being controlled by bactericidal tests. The fractions obtained at different temperatures have different coefficients against *B. typhosus*, the higher fractions, which distil at 200–266° C. and consist of aromatic hydroxy compounds, having the stronger germicidal action. The various fractions can be used as disinfectants either in the concentrated state, in solution in an organic solvent, in suspension in water, in emulsion in mucilage, or made up into a solid form.—J. H. J.

*Schweinfurt Green or other compounds of copper and arsenic: Process for rendering* — soluble in water. Chem. Fabrik Schweinfurt G. m. b. H. Fr. Pat. 471,466, Apr. 29, 1914. Under Int. Conv., Aug. 21, 1913.

THE compound is mixed with a nitrogenous substance, such as gelatin or protein substances or their derivatives, and with a caustic alkali or alkaline earth hydroxide and water, and, if necessary, heated until the solution has a blue tint. The liquid contains only traces of free ammonia and is suitable for a plant insecticide.—C. A. M.

*Cleaning and disinfecting liquids. [Paint removers]* I. L. Halman. Fr. Pat. 471,747, May 2, 1914. Under Int. Conv., May 7, 1913.

A CAUSTIC alkali, an ammonium salt, and an alkali carbonate are dissolved successively in water, and an alcohol is added, preferably in the proportion, 9.8% KOH, 2.5% NH<sub>4</sub>Cl, 1.25% K<sub>2</sub>CO<sub>3</sub>, 80–82% water, and 4.95–5% alcohol.—F. SODN.

*Electrochemical treatment of liquids. [Water softening.]* C. P. Landreth, Philadelphia, U.S.A. Eng. Pat. 3181, Feb. 6, 1914. Under Int. Conv., Feb. 21, 1913.

SEE Fr. Pat. 468,277 of 1914; this J., 1914, 971.

*Liquid-steriliser.* V. Henri, A. Helbronner, and M. von Recklinghausen, Paris, Assignors to The R.E.V. Co. U.S. Pat. 1,132,265, March 16, 1915. Date of appl., Feb. 26, 1910.

SEE Addition of March 1, 1910, to Fr. Pat. 400,602 of 1909; this J., 1910, 1129.

*Water and other liquids: Apparatus for the treatment of* — by ultra-violet rays. V. Henri, Paris, and A. Helbronner and M. von Recklinghausen, Suresnes, France, Assignors to The R.E.V. Co. U.S. Pat. 1,132,266, March 16, 1915. Date of appl., Nov. 10, 1913.

SEE Eng. Pat. 25,509 of 1909; this J., 1910, 1471.

*Apparatus for detecting and estimating the impurities and dissolved matter in water and other liquids.* Eng. Pat. 12,735. See XXIII.

## XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

*Opium; Influence of mould fungi on the alkaloid-content of —.* O. v. Friedrichs. Z. physiol. Chem., 1914, 93, 276—282.

PETRI dishes containing moistened opium, in some cases mixed with 10% of lactose, were inoculated with four different moulds and incubated at 18°—22° C. for 20 hours. In all cases profuse mycelial growth was observed, but two of the organisms, *Penicillium viridicatum* and *Citromyces glaber*, were without any action on the alkaloids determined (morphine, narcotine, and codeine). *Aspergillus niger* did not attack morphine but destroyed small quantities of narcotine and codeine. *Aspergillus Ostianus*, found on opium from the Levant, decomposed all three to some extent, but morphine only slightly. Growth of moulds on pharmaceutical preparations of opium is therefore not likely to reduce their content of alkaloids to any considerable extent.—J. H. L.

*Digitalis leaves; Physiological valuation of —, and the enzymes of digitalis.* Rapp. Apoth.-Zeit., 1914, 29, 860, 865—867. Z. angew. Chem., 1915, 28, Ref., 19.

THE physiological value of digitalis preparations can be determined accurately only by a biological process. The author prefers Halc's method to that of Focke. The guaiacum reaction is useful only as affording indications of the method of drying and preservation. In moist digitalis leaves the physiological value diminishes owing to enzyme action. The quantity of sugars formed in the digitalis plant by enzyme action is not an exact measure of the amount of digitalis glucosides lost thereby. A digitalis preparation free from enzymes can be obtained by heating the drug for 10 minutes in an autoclave at 105° C., but the secondary gastric effects produced by digitalis powder are observed also with the enzyme-free preparation.—A. S.

*Cusparine; Isomerisation and decomposition of —. Investigations on the alkaloids of Angostura.* J. Troeger and W. Müller. Arch. Pharm., 1914, 252, 459—480. Z. angew. Chem., 1915, 28, Ref., 19. (See also this J., 1910, 294; 1911, 152; 1912, 1050.)

CUSPARINE,  $C_{18}H_{14}NO_2 \cdot OCH_3$ , m. pt. 93° C. is a quinoline derivative. By the action of moist silver oxide or potassium hydroxide on its methiodide, ethiodide, or propiodide, isocusparine,  $C_{18}H_{14}O_2 \cdot NCH_3$ , m. pt. 194° C., is produced. When cusparine is heated in a current of dry hydrogen chloride, pyrocusparine,  $C_{16}H_{11}NO_2$ , m. pt. 255° C., is formed. This yields a nitro-derivative,  $C_{16}H_{11}NO_2(NO_2)$ , m. pt. 283° C., when treated with dilute nitric acid.—A. S.

*Calcium-theobromine; Crystallised —.* L. Rousseau. Comptes rend., 1915, 160, 363—365.

THEOBROMINE (2 mols.) and calcium oxide (1 mol.) are heated together in the presence of water, and the fine long needles obtained on cooling are dried over sulphuric acid. The product,  $(C_7H_7N_3O_2)_2 \cdot Ca_2O \cdot 9H_2O$ , is soluble in 64 parts of water at 16° C., and in 14 at 100° C.; and in 625 parts of alcohol at 90° C., being thus 25 times

more soluble in cold water, 10 times in boiling water, and 7 times in boiling alcohol than theobromine. Carbonic and other acids liberate the theobromine in the colloidal state, and this is probably the cause of the rapidity and intensity of the diuretic effect of the salt when it comes into contact with gastric juice in the stomach.—J. P. O.

*Pepsin; Use of edestin in the determination of —.* R. Delaunay and O. Bailly. Bull. Sci. Pharmacol., 1915, 24. Pharm. J., 1915, 94, 389.

EDESTIN, a vegetable globulin from hemp seed, can be advantageously substituted for fibrin in determining the activity of pepsin. It is prepared by extracting bruised, fat-free hemp seed with 10% sodium chloride solution, in which edestin is readily soluble and from which it can be obtained either by the addition of large excess of water, or by removing the salt by dialysis, or in a crystalline state by strongly cooling the hot solution. Edestin is insoluble in pure water but soluble in dilute solutions of neutral salts and in 2.5% hydrochloric acid, from which latter solution it is precipitated by nitric acid. 0.2 gm. of pepsin of the strength of the French Pharmacopoeia completely digests the edestin in 20 c.c. of a 0.5% solution in 2.5% hydrochloric acid in 15 minutes at 50° C. The presence of undigested edestin is shown by the turbidity produced by the addition of 30 drops of nitric acid to the cooled solution.—T. C.

*Cholesterol; Oxidation of — by the blood tissue.* J. Lifschütz. Z. physiol. Chem., 1914, 93, 209—227.

EXPERIMENTS have shown that cholesterol is oxidised to some extent on digestion at 60° C. for several days with glacial acetic acid and dried fat-free blood, thus confirming the author's view that in the body the oxidation of cholesterol takes place in the blood.—J. H. L.

*Eucalyptus globulus of California; Oil of —.* C. E. Burke and C. C. Scaglione. J. Ind. Eng. Chem., 1915, 7, 206—209.

LARGE quantities of *Eucalyptus globulus* oil could be produced in California and other parts of the Pacific coast where the tree is grown for timber, but the oil does not fulfil the requirements of the U.S. Pharmacopoeia. It has sp. gr. 0.9052 at 20° C.,  $[\alpha]_D^{20} = -14.42$ ,  $n_D^{20} = 1.46053$ , and is insoluble in 70% alcohol, differing notably from the Australian oil. The Californian oil contains the same constituents as the Australian oil, but in different proportions. It contains butyric, isovaleric, and capronic aldehydes, 6; pinene, 21—22; cineol, 47; alcohols (eudesmol, globuol), 23%; the high content of pinene is the chief cause of the difference in properties from the Australian oil. In distilling the oil the burrs should be separated from the leaves, as the oil from the former is inferior to the leaf oil.—A. S.

*Anised oil; Quantity of iodine absorbed by —.* E. Morin. Ann. Chim. Analyt., 1915, 20, 49—52.

It was found that pure anised oil absorbed iodine in the average proportion of 1.6961 gm. per gm. of oil, when the absorption was determined by Hübl's method, using a solution of the oil in 50% alcohol and allowing the reaction to proceed for 3 hours. The quantity of iodine absorbed was not, however, constant; it varied with the amount of oil in the solution, e.g., from 1.651 gm. per gm. of oil, when a 0.08% solution of the latter was employed for the determination, to 1.7356 gm. in the case of a 0.12% solution.—W. P. S.

*Camphor production in the United States.* Oil, Paint, and Drug Rep., March 29, 1915.

IMPORTS of camphor into the United States from Japan during 1914 amounted to over 5,000,000 lb., and in view of the tendency of the Japanese monopoly to demand high prices and to encourage home consumption, increasing efforts are being made to develop camphor forests in the southernmost portions of the United States and also to produce camphor synthetically from a turpentine base. Many difficulties, however, are still being encountered and, despite many years of experimental work and an enormous outlay of money, the results attained to date have been meagre, and have appeared far from warranting the expenditure already made.

Recent activities in camphor forestry include the entrance into this field of three new enterprises, two of which are conducted in Florida and one in Texas. A pioneer enterprise, backed by the manufacturers of nitrocellulose products, had previously invested heavily in these trees and, a year ago, added 500 acres of new camphor trees; now it has many thousands of young trees in its nursery. The company, like others which have more recently embarked upon the industry, was encouraged by the suggestion of the United States Department of Agriculture, which repeatedly pointed out the desirability and practicability of producing the natural product in the United States. It was soon discovered that the Government's statistics on the growth, development, and yield of camphor trees were both deficient and inaccurate and all available figures on production had to be revised materially. Nevertheless, this enterprise, whose camphor forest is at Satsuma Heights, Fla., has already obtained 10,000 lb. of crude camphor from its trees and is now looked upon as a promising venture, although the returns from the investment have fallen far short of the originally sanguine expectations of its backers.

Of the three other enterprises mentioned, the Florida Essential Oils Company has the nucleus of a camphor forest at Green Cove Springs, Fla., and has recently bought 10,000 acres of land in that locality, in which it is planning to set out thousands of new camphor trees. St. Mary's Florida Colony Company has lately purchased 10,000 acres of land at Glen St. Mary, Fla., and expects to utilise 2,000 acres of this property in the near future for camphor tree growing. The Alvin Japanese Nursery Company has acquired 100 acres of land for camphor tree growing near Alvin, Tex., and reports that 500 acres of land close to its property are already devoted to a small forest of these trees.

The greatest handicap with which these enterprises have to contend is the relatively small yield of the new trees. Many of the Japanese and Chinese trees are 50 to 100 years old and some of them from 200 to 500 years old; even from comparatively young trees, there have been obtained yields valued at \$3,000 to \$5,000 each.

The Schering interests in Germany have long since succeeded in making a comparatively large quantity of synthetic camphor from a turpentine base, which meets all commercial and pharmacopoeial requirements, but have been unable to produce it cheaply enough to compete with the natural product except when prices have been abnormally high. This has also been the experience of the numerous American experimenters in this field. Recently, however, the American Camphor Corporation, of Philadelphia, has contended that it can produce enough gum camphor in this way to meet the requirements of the manufacturers of nitro-cellulose compounds as well as the drug trade. However, it seems that the makers are not yet in a position to make camphor in sufficient quantities, although some of the refined synthetic

gum made by this company has been employed by the drug trade.

*Alcohol in pharmaceutical preparations; Determination of —.* Reuss. Pharm. Zentralh., 1915. Pharm. J., 1915, 94, 489.

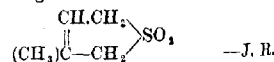
RICHTER's method is modified as follows:—25 c.c. of the preparation, 25 c.c. of 20% sodium chloride solution, and 15 c.c. of petroleum spirit (b. pt. 40°–55° C.) are shaken together in a separator for one or two minutes; the salt solution containing the alcohol is separated, and after some time a further layer of alcohol in salt solution is formed, which is also separated. The traces of alcohol remaining in the petroleum spirit are shaken out with fresh salt solution, the alcoholic extracts are distilled, after neutralisation if volatile acids are present, and the alcohol is collected in a pycnometer and determined in the usual manner.

*Urease of soya beans, and its application to the determination of urea.* F. Elgenberger. Z. physiol. Chem., 1915, 93, 370–377.

THE urease present in soya beans may be used for the determination of urea in urine. The urease solution is added to the urine and a current of air drawn through the mixture, the ammonia formed being absorbed in standard acid. The whole of the ammonia is liberated from the urea in about 1 hour, and the results obtained agree well with those found by the Kjeldahl and other methods. The urease solution is prepared by mixing an aqueous extract of the beans with a large excess of acetone, separating the precipitate, and dissolving it in ten times its weight of water to which is added, for every gram. of the precipitate, 0.6 gram. of dipotassium phosphate and 0.4 gram. of monopotassium phosphate.—W. P. S.

*Isoprene; A crystalline compound of — with sulphur dioxide.* G. de Bruin. Koninkl. Akad. van Wetenschappen, Amsterdam, June 27, 1914. Chem.-Zeit., 1914, 38, 1205.

AFTER keeping in a sealed tube at the ordinary temperature for two days, a mixture of isoprene and liquid sulphur dioxide deposited white crystals of an addition product, melting at 62.5° C., and probably possessing the structure:



*Halogens; Catalytic addition of the — (to unsaturated organic compounds).* L. Bruner and J. Fischler. Z. Elektrochem., 1914, 20, 84. Chem.-Zeit., 1915, 39, Rep. 57.

IODINE and antimony tribromide act as catalysts in presence of bromine not only in substitution reactions, but also in addition reactions with such substances as acetylene dichloride and ethyl cinnamate; the relation between the amount of catalyst and the reaction-velocity is different in the two classes of reaction.—J. R.

*Chemical action of light.* G. Ciamician and P. Silber. Ber., 1915. Apoth.-Zeit., Mar. 6, 1915. Pharm. J., 1915, 94, 489.

NICOTINE in aqueous solution exposed to light for six months, was converted by autoxidation into resinous compounds and oxynicotine, which was further oxidised to nicotinic acid and methylamine. Similarly piperidine is converted into a base containing oxygen, and formic and glutaric acids are formed. Copper benzoate suspended in acet-aldehyde and exposed to light for seven months, was reduced to metallic copper, which was separated partly as a precipitate and partly in the

form of a mirror: benzoic acid is liberated, and apparently acetic acid is formed.

**Formaldehyde; Determination of**—and of hexamethylenetetramine in formalin pastilles. W. Stäwe. Arch. Pharm., 1914, 252, 430–435. Z. angew. Chem., 1915, 28, Ref., 18.

THE solution containing formaldehyde is added to freshly-prepared Nessler's solution, whereupon reduction to metallic mercury occurs. After acidifying with dilute acetic acid, the mercury is dissolved by treatment with excess of *N*/10 iodine solution, and the excess titrated with *N*/10 thio-sulphate. The process may also be used for the determination of hexamethylenetetramine, *e.g.* in formalin pastilles.—A. S.

**Acid secretion of the gram plant, *Cicer arietinum*.** Sahasrabudde. See XVI.

**Determination of the iodine value of alcoholic liquors by Hübl's method. Iodine value of essential oils.** Marcille. See XVIII.

#### PATENTS.

**Aminophenyl arsenic compound.** A. H. C. Heitman, Assignor to Parke, Davis and Co., Detroit, Mich. U.S. Pat. 1,110,279, Dec. 1, 1914. Date of appl., April 5, 1913.

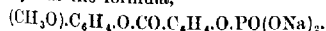
AROMATIC amino compounds in which an amino group is combined with at least one carbo-ethoxy group, are prepared by treating aminophenyl arsenic derivatives with carbo-ethoxy compounds such as ethyl chlorocarbonate, then nitrating, and reducing the nitro group. Examples mentioned are carbo-ethoxy-*p*-aminophenylarsenoxide,  $C_6H_5O.CO.NH.C_6H_4.AsO$ , and carbo-ethoxy-4,5-diaminophenylarsenoxide. The compounds are claimed as specifics, *e.g.* for hog cholera.—F. Sp.

**Acetylsalicylic acid compounds; Derivatives of**—W. Hiemenz, Elberfeld, Germany. Assignor to Synthetic Patents Co., New York. U.S. Pat. 1,122,201, Dec. 22, 1914. Date of appl., Sept. 3, 1914.

ANTIPYRETIC and antineuralgic compounds of the general formula,  $RO.CO.R'O.CO.R''$  (in which RO is the radical of salicylic acid or a derivative thereof, R' is an aliphatic radical, and R'' is any organic radical) are claimed. Example:—Acetyl-glycolyl chloride is condensed with salicylic acid in the presence of dimethylaniline diluted with benzene, forming acetylglycolylsalicylic acid,  $COOHC_6H_4O.CO.CH_2O.CO.CH_3$ , m. pt. 103° C. The following compounds are also mentioned:—Acetylglycolyl-*m*-cresotinic acid (m. pt. 108°); acetylglycolyl-*p*-cresotinic acid (m. pt. 151°); acetylglycolylchlorosalicylic acid (m. pt. 135°); acetylglycolyl-iodosalicylic acid (m. pt. 144°); acetyl-lactyl-*p*-cresotinic acid (m. pt. 128°); cinnamoylglycolylsalicylic acid (m. pt. 135°), and anisoylglycolylsalicylic acid (m. pt. 123° C.)—F. Sp.

**Carboxylarylyphosphoric acids; Esters of**—M. Engelmann, Elberfeld, Germany. Assignor to Synthetic Patents Co., New York. U.S. Pat. 1,125,081, Jan. 19, 1915. Date of appl., May 12, 1914.

CLAIM is made for compounds of the type,  $ROOC.Ar.O.PO(OH)_2$ , and more particularly for the guaiacol ester of *p*-carboxylphenylphosphoric acid, m. pt. 182° C., the sodium salt of which probably has the formula,



Other examples are the iso-cresyl ester (m. pt. 179°) and the thymol ester (m. pt. 163° C.) of *p*-carboxy-

phenylphosphoric acid. The compounds are prepared by the interaction of alcohols, phenols, phenol-alcohols, or hydroxy acids with the halogen-carbonyl-arylyphosphoric acid halides produced by the action of phosphorus halides on aromatic hydroxy acids. They are said to be valuable remedies against infectious diseases. They are crystalline, odourless products soluble in alcohol and sparingly soluble in water; their salts are mostly soluble in water.—F. Sp.

**Perfumes; Process of obtaining**—by means of solvents. Lauther Fils. Fr. Pat. 472,250, July 30, 1913.

RAPID evaporation of the solvent at low temperatures is secured by projecting the solution of the perfume in a spray against a warm surface in a special still, with or without vacuum. The vapours of the solvent pass off and are condensed, and the concentrated solution of the perfume is drawn off, either continuously or intermittently, at the bottom of the still.—F. Sp.

**Hydrastinine derivatives; Preparation of**—E. Merck. Ger. Pat. 279,194, Dec. 24, 1912.

DIHYDROISOQUINOLINE bases (hydrastinine derivatives) are prepared by treating homopiperonylamine derivatives of the general formula,  $CH_2O_2 : C_6H_3.CH_2.CH(alkyl).NR.CH_2O$  (R = hydrogen, alkyl, or aralkyl), with acid condensing agents, such as phosphorus pentoxide or pentachloride, aluminium chloride, or zinc chloride. When R = hydrogen, the 6,7-methylenedioxy-3,4-dihydro-3-alkylisoquinolines obtained are subsequently converted into *N*-alkyl or *N*-aralkyl derivatives.—A. S.

***o*-Methylcoumaranes; Preparation of**—Farben-fabr. vorm. F. Bayer und Co. Ger. Pat. 279,864, Oct. 9, 1913.

*o*-ALLYLPHENOLS having the allyl group united to a carbon atom are treated with a hydro-halogen acid or other acid condensing agent, and the products distilled *in vacuo*. The *o*-methylcoumaranes thus obtained are colourless liquids useful for pharmaceutical purposes.—A. S.

**Ferrous salts of aromatic hydroxy-carboxylic acids and their derivatives; Preparation of acid**—M. Claass. Ger. Pat. 279,865, Jan. 29, 1914.

ALKALI salts of hydroxybenzoic acids or of their derivatives, nuclear homologues or substitution products, are treated in hot aqueous solution with ferrous salts in presence of a small quantity of a reducing agent, such as sodium hydrosulphite; on cooling, the acid ferrous salt, *e.g.*, acid ferrous salicylate, crystallises. The products may be used as antiseptics.—A. S.

**2-Halogen-2-methylbutane; Preparation of**—Badische Anilin und Soda Fabrik. Ger. Pat. 279,955, Sept. 10, 1913.

THE fraction distilling up to about 45° C., resulting from the cracking of high-boiling hydrocarbons, is treated with a hydro-halogen acid. The 2-halogen-2-methylbutane so obtained is purified by distillation. It can be used for the synthesis of isoprene.—A. S.

**Mercury compounds of tyrosine and its derivatives; Preparation of**—F. Hoffmann-La Roche und Co. Ger. Pat. 279,957, Sept. 25, 1913.

ALKALINE solutions of tyrosine or its derivatives are treated with mercuric compounds at the ordinary temperature. The products are sparingly soluble in water but readily soluble in alkalis: the alkaline solutions change to jellies when kept for

a long time. Mercuric sulphide is precipitated gradually from the cold solutions by ammonium sulphide.—A. S.

*Mercurised aminoarylsulphonic acids; Preparation of* —. Chem. Fabr. von Heyden A.-G. Ger. Pat. 281,009, April 24, 1914.

MERCURY aminoarylsulphonates, or mixtures of aminoarylsulphonic acids with mercury compounds capable of reacting with the acids to form salts, are heated until the organic mercury compound becomes soluble in alkali. In the products obtained, e.g. sodium mercuri-*m*-aminobenzene-sulphonate, sodium mercuri-aminophenol-sulphonate, and acid sodium mercuri-*m*-aminobenzoate, the mercury is more firmly combined than in corresponding compounds not containing an amino group. When sodium mercuri-*m*-aminobenzenesulphonate, for example, is treated with ammonium sulphide solution, darkening is observed only after 24 hours. Introduction of a hydroxyl group renders the mercury less firmly combined.—A. S.

*Alkyl esters of triacetylgallic acid; Preparation of* —. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 279,958, March 13, 1913.

THE alkyl esters of gallic acid, with the exception of the methyl ester, are acetylated, or triacetylgallic acid is converted into its alkyl esters, with the exception of the methyl ester, by the usual methods. The products are of value as astringents.—A. S.

*Hydro-derivative of colchicine; Preparation of a* —. F. Hoffmann-La Roche und Co. Ger. Pat. 279,999, June 10, 1913.

COLCHICINE is treated with hydrogen in presence of finely divided palladium or a colloidal solution of palladium. The product, probably tetrahydro-colchicine, is less toxic than colchicine.—A. S.

*p*-Aethylaminophenol alkyl ethers; *Preparation of [hydroxy] derivatives of* —. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 280,025, April 13, 1913.

COMPOUNDS of the general formula, (acyl)-R.N.C<sub>6</sub>H<sub>4</sub>.OR, (R = hydrogen, alkyl, acyl, aryl, or aralkyl; R<sub>1</sub> = alkyl with one or more substituted hydroxy groups), are obtained by treating *N*-acyl-*p*-aminophenols with polyhydric alcohols or their anhydrides or with halogen-substituted alcohols, or by acylating the amino group of *O*-hydroxyalkyl ethers of *p*-aminophenol. They exhibit pronounced analgesic action but are only slightly antipvretic, and are less active than phenacetin in forming hæmoglobin.—A. S.

*Phosphorus compounds of derivatives of higher fatty acids; Preparation of lipid* —. F. Hoffmann-La Roche und Co. Ger. Pat. 280,411, Dec. 4, 1913.

LIPID phosphorus compounds, which are readily resorbed, are obtained by the action of hypophosphorous acid or its salts on higher keto-fatty acids or their derivatives, e.g. esters or amides of the acids, diketeto-acids, or hydroxyketo-acids. The new compounds when in the form of free acids are sparingly soluble in water, insoluble in petroleum spirit, and readily soluble in glacial acetic acid, ether, and alcohol; the alkali and ammonium salts are readily soluble in water. The compounds are not decomposed by bases, even on boiling. They possess reducing properties corresponding to those of phosphorous acid.—A. S.

*Hydrolecithin; Preparation of* —. J. D. Riedel A.-G. Ger. Pat. 280,695, March 1, 1914. Addition to Ger. Pat. 250,998 (this J., 1913, 507).

LECITHIN in aqueous colloidal solution or suspended in water is treated with hydrogen or a gaseous mixture containing hydrogen in presence of a finely-divided or colloidal metal of the platinum group. Other animal or vegetable phosphatides can be hydrogenised in a similar manner. (See also Ger. Pat. 279,200; this J., 1915, 250.)—A. S.

*Morphine; Preparation of alkyloxymethyl ethers of* —. C. Mannich. Ger. Pat. 280,972, June 15, 1913.

ALKYLOXYMETHYL ethers of morphine are obtained by the interaction of alkali compounds of the alkaloid and halogen alkyl ethers of the general formula, hal.CH<sub>2</sub>.O.alkyl. The methoxymethyl ether of morphine has a physiological action stronger than that of the alkyl ethers of morphine but weaker than that of morphine itself. It may be used for the preparation of other morphine derivatives, being readily converted into *N*- or *O*-alkyl derivatives. When heated for a short time with sulphurous acid the methoxymethyl group is removed.—A. S.

*Chondroitin-sulphuric acid; Preparation of soluble salts of* —. J. D. Riedel A.-G. Ger. Pat. 280,974, Dec. 19, 1913.

A MIXTURE of concentrated solutions of equivalent quantities of a salt of a heavy metal and an alkali salt of chondroitin-sulphuric acid is dialysed against water, and the resulting solution of the heavy metal salt of chondroitin-sulphuric acid is evaporated to dryness at a moderate heat or treated with a precipitant such as alcohol or ether. The products are useful for treating affections due to parasites.—A. S.

*Esters of 8-hydroxyquinoline; Preparation of [the salicylic and acetylsalicylic] esters of* —. R. Wollenstein. Ger. Pat. 281,007, June 5, 1913.

THE salicylic and acetylsalicylic esters of 8-hydroxyquinoline are prepared by treating it with the corresponding acid chlorides. They are of value therapeutically by reason of their effect on the metabolism of purine derivatives.—A. S.

*Bile; Process for obtaining a therapeutically active preparation from* —. R. Nöhning. Ger. Pat. 280,108, June 14, 1913.

BILE, preferably diluted with water, is treated with acid, the precipitated colouring matter filtered off, and the solution treated with alkali to precipitate the active substance. The product is toxic towards pathologically altered organisms but practically non-poisonous to normal organisms.—A. S.

*Lithium acetylsalicylate; Process of manufacturing* —. A. Busch, Brunswick, Assignor to J. A. Wülfing, Berlin, Germany. U.S. Pat. 1,129,953, March 2, 1915. Date of appl., Feb. 25, 1914.

SEE Eng. Pat. 9266 of 1913; this J., 1914, 613.

*Protocatechuic acid and protocatechuic aldehyde; Preparation of* — from piperonal. L. Schmidt. Fr. Pat. 471,986, May 8, 1914. Under Int. Conv. Sept. 15, 1913.

SEE Ger. Pat. 278,778 of 1913; this J., 1915, 249.

**XXI.—PHOTOGRAPHIC MATERIALS AND PROCESSES.**

*Solubility of silver chloride.* Glowczynski. See VII.

**PATENTS.**

*Printing photographic negatives or positives on sensitive films of all kinds; Method of—*, A. Schwarz and W. Riebensahm. Ger. Pat. 279,232, Feb. 10, 1914.

A substance, such as quartz, which possesses a high degree of transparency for the chemically active ultra-violet rays, is used as a support for the film on which the negative or positive is produced. Prints can then be obtained in a fraction of the time required when a glass plate is used.

—A. S.

*Polychrome screens; Preparation of—*, M. Petzold. Ger. Pat. 279,932, June 26, 1913.

A red and a green acid or azo dyestuff, each dissolved in a chromate solution, are printed successively, in juxtaposition, on a gelatin plate, and the intervening spaces are then coloured with a blue dyestuff of the rosaniline series. The chromate is reduced by the gelatin and forms insoluble or sparingly soluble colour lakes with the red and green dyestuffs.—A. S.

**XXII.—EXPLOSIVES; MATCHES.****PATENTS.**

*Explosive mixtures containing chlorates or perchlorates.* E. C. R. Marks, London. From Pala Companhia Himalavite, Lisbon. Eng. Pat. 29,507, Dec. 22, 1913.

POTASSIUM, sodium, or ammonium chlorate or perchlorate (76 to 82%) is mixed with a solid combustible substance such as starch or sawdust (8 to 21%), a liquid combustible substance such as mineral or vegetable oil (3 to 8%), and finely divided aluminium or other readily oxidisable metal, or an aluminium alloy, iron carbide, or ferrosilicon (2 to 8%), together with less than 2% of a "detonating compound," such as a permanganate or chromate, or sulphur or sulphur compound.—C. A. M.

*Explosive; Manufacture of a new—, and products comprising the same.* F. E. Matthews, London. Eng. Pats. 6447 and 6448, March 13, 1914.

CLAIM is made for nitro-isobutyl-glycerol trinitrate,  $\text{NO}_2\text{C}(\text{CH}_2\text{ONO}_2)_3$ , obtained by nitrating nitro-isobutyl-glycerol. It is very stable to heat, and, in many cases, may be used as a substitute for nitroglycerin, e.g., in admixture with kieselguhr nitro-cotton, etc.—C. A. M.

*Explosive containing liquid air or oxygen and lampblack.* G. Claude, Assignor to Soc. l'Air Liquide (Soc. anon. pour l'Etude et l'Exploit. des Proc. G. Claude), Paris. U.S. Pat. 1,131,994, March 16, 1915. Date of appl., Dec. 20, 1913.

SEE Fr. Pat. 463,876 of 1912; this J., 1914, 376.

**XXIII.—ANALYTICAL PROCESSES.**

*Sulphuric acid drying vessel; New form of—*, Earl of Berkeley, and E. G. J. Hartley. Phil. Mag., 1915, 29, 609—613.

SULPHURIC acid is as efficient for drying gases as phosphorus pentoxide, and it is moreover not

necessary to bubble the gas through the acid but suffices to lead it over the surface, thus avoiding the risk of introducing acid spray into the stream of gas and uncertain changes in its volume. The drying vessel described consists of four horizontal tubes, 22 cm. long, and 2 cm. diam., connected together in series so as to form four separate compartments, which are each about half filled with sulphuric acid (about 70 c.c. in all). The two ends of the series of tubes terminate in vertical tubes with glass stoppers and detachable mercury cups. In tests with this apparatus, 600 litres of air saturated with water vapour at 30° C. was completely dehydrated after a week's run, and a phosphorus pentoxide tube placed in series beyond the sulphuric acid tube only gained 0.0001 grm. during the whole experiment, whilst the acid had absorbed 5.52 grms., nearly all of which was taken up in the first (inlet) branch. After running for three days at 30° C., only about 0.0001 grm. of sulphuric acid had been carried over. An alternative method for drying air is to use stick potash, which is also nearly as efficient. Pure anhydrous copper sulphate will absorb about 0.05% of its weight of water-vapour, and is a very efficient drying agent for air containing little more than traces of moisture; it can be used again after heating to 210°—220° C. in a current of air.—G. F. M.

*Iron, aluminium, chromium, manganese, and zinc; Methods for separating and determining—*, G. Van Pelt. Bull. Soc. Chim. Belg., 1914, 138. Ann. Chim. Analyt., 1915, 20, 68—70.

A SOLUTION of the chlorides of iron, aluminium, chromium, manganese, and zinc is diluted to 200—300 c.c. and heated on a water-bath with a few drops of nitric acid and 2 grms. of ammonium persulphate, until the chromium is oxidised completely. The solution is cooled and poured into a solution containing ammonium chloride, concentrated hydrogen peroxide, and an excess of ammonia; the mixture is warmed, the hydroxides of iron, aluminium, and manganese are then collected, washed, dried, and fused with a mixture of equal weights of sodium carbonate and potassium nitrate. The cooled mass is extracted with water, and the insoluble ferric oxide collected and weighed. The filtrate, containing aluminate and manganate, is concentrated on a water-bath, acidified, and treated with hydrogen peroxide to convert the manganate into manganese salt, diluted to 250 c.c., treated with an excess of sodium hydroxide, and the manganese precipitated by hydrogen peroxide. The manganese hydroxide is separated, the filtrate is acidified with hydrochloric acid, and the aluminium precipitated by adding ammonia to the boiling solution. The first filtrate, containing the chromium and zinc, is acidified, concentrated, and treated with hydrogen peroxide. The residue is dissolved in water containing ammonium chloride, the solution boiled, and the chromium precipitated by ammonia. Zinc is precipitated in the filtrate from the chromium hydroxide by boiling with sodium carbonate until all ammonia has been expelled.—W. P. S.

*Selenium; Reaction for identifying traces of—*, G. Denigès. Ann. Chim. Analyt., 1915, 20, 59—61.

A SMALL quantity of the material is boiled with a few drops of concentrated nitric acid, then diluted with an equal volume of water and treated with a solution of mercurous nitrate containing nitric acid. If selenium is present, a characteristic crystalline precipitate of mercurous selenite is obtained. When dealing with traces of selenium, the test may be carried out on a microscope slide. (See also page 421.)—W. P. S.

*Molybdc acid [used in analysis]; Recovery of*—  
W. D. Brown. *J. Ind. Eng. Chem.*, 1915, 7,  
213—214.

THE solution containing molybdc acid is heated to boiling and treated with five times the theoretical quantity of sodium phosphate, the yellow precipitate is filtered off, washed, dried, and 210 grms. of it is mixed with 800 c.c. of water and 600 c.c. of ammonia solution and treated with 35 grms. of magnesium nitrate dissolved in 100 c.c. of water. The precipitated ammonium magnesium phosphate is filtered off and washed with 100 c.c. of water or dilute ammonia solution, and the filtrate and washings are added to 1900 c.c. of nitric acid (1:1), giving 3500 c.c. of ammonium molybdate solution containing the usual amounts of ammonia and nitric acid.—A. S.

*Refrigeration in toxicological analysis; Use of*—  
G. A. Le Roy. *Comptes rend.*, 1915, 160, 313—314.

To facilitate the reduction of viscera, etc., to a homogeneous condition, as a preliminary to extracting alkaloids, they are placed in a freezing chamber at  $-6^{\circ}$  to  $-10^{\circ}$  C. for 10 to 24 hours. The congealed mass may then be reduced to a fine state of division by the usual method.—F. W. A.

*Combustion calorimetry and the heats of combustion of sucrose, benzoic acid, and naphthalene.* Dickinson. See IIA.

*Separation of gases by fractional distillation in a vacuum at low temperatures. Rapid method of fractionating gases at low temperatures.* Burrell and Robertson. See IIA.

*Analytical distillation of petroleum.* Rittman and Dean. See IIA.

*Apparatus for determining the melting point of paraffin wax.* Small. See IIA.

*Bolometric method of determining the efficiencies of radiating bodies [gas fires].* Bone and others. See IIB.

*Chemical analysis of paper.* Bromley. See V.

*Reactions of selenic and telluric acids and their salts.* Denigès. See VII.

*New method of valuing hydrosulphites.* Knecht. See VII.

*Action of metals upon [and detection and determination of] mercuric cyanide.* Pertusi. See VII.

*Precipitation of zinc and manganese by ammonium sulphide.* Seeligman. See VII.

*Determination of the composition of argon-nitrogen mixtures [for filling half-watt lamps] by liquid air.* Hamburger and Filippo. See VII.

*Sensitive method for examining some optical qualities of glass plates.* Earl of Berkeley, and Thomas. See VIII.

*Determination of the heat-conductivity of refractory building materials.* Ilcyn. See IX.

*Determination of copper in steel.* Brown. See X.

*Determination of zinc in ores and pyrites cinder.* Rubricius. See X.

*Rapid analysis of alloys [matte, slags, etc.] for tin, antimony, and arsenic.* Stief. See X.

*Determination of unsaponifiable matter in greases.* Twitchell. See XII.

*Examination of floor polishes.* Besson and Jungkuz. See XIII.

*Valuation of granular substances [pigments, etc.] by counting the particles.* Kühn. See XIII.

*Determination of total sulphur in rubber.* Tuttle and Isaacs. See XIV.

*Distinction and detection of tanning materials and cellulose extract in leather.* Lauffman. See XV.

*Determination of ammonia in soils.* Potter and Snyder. See XVI.

*Determination of soil carbonates.* MacIntire and Willis. See XVI.

*The direct and invert polarisation of pure sucrose.* Walker. See XVII.

*Measurement of the fermentative action of yeast by means of the liquid interferometer.* Wolff. See XVIII.

*Determination of the iodine value of alcoholic liquors by Hubl's method. Iodine value of essential oils.* Marceille. See XVIII.

*Freezing point of milk considered in relation to the detection of added water.* Monier-Williams. See XIX.

*Determination of the total fatty acids and other ether-soluble constituents of feeding stuffs.* Rather. See XIX.

*Use of edestin in the determination of pepsin.* Delaunay and Bailly. See XX.

*Physiological valuation of digitalis leaves and the enzymes of digitalis.* Rapp. See XX.

*Urease of soya beans and its application to the determination of urea.* Eigenberger. See XX.

*Determination of formaldehyde, and of hexamethylenetetramine in formalin pastilles.* Stüwe. See XX.

*Determination of alcohol in pharmaceutical preparations.* Reusz. See XX.

#### PATENTS.

*Water and other fluids; Apparatus for the detection and estimate of impurities and dissolved matter in*—, Evershed and Vignoles, Ltd., and W. Clark, London. Eng. Pat. 12,735, May 23, 1914.

IN apparatus for determining the amount of impurities in water and other fluids by measuring the electrical conductivity (see Eng. Pat. 23,706 of 1907; this J., 1908, 1036), a thermometer fitted in a sliding bearing is inserted in the tube containing the electrodes; the diameter of the thermometer is only slightly less than the bore of the conductivity tube. By altering the position of the thermometer according to the temperature of the liquid, and thus modifying the dimensions of the column of liquid through which the current passes, the conductivity may be read directly and no temperature correction need be applied. A scale and a pointer are provided to denote the position of the thermometer.—W. P. S.

*Process and apparatus for determining the degree of impurity of water and other liquids.* Fr. Pat. 471,351. See XIXb.

## XXIV.—MISCELLANEOUS ABSTRACTS.

*Enzymic decomposition of hydrogen peroxide.* P. Waentig and O. Steche. *Z. physiol. Chem.*, 1914, 93, 228—234.

It has already been demonstrated (*Z. physiol. Chem.*, 1913, 83, 315) that the activity of catalase towards hydrogen peroxide is destroyed by trypsin, and the conclusion has been drawn that the former enzyme is a protein. It is now shown that the peptolytic enzyme, erepsin, exerts a similar destructive action on catalase, and, although erepsin preparations are not free from tryptic enzymes, the action referred to is probably due to the peptolytic components.—J. H. L.

## Trade Report.

*Patents, Designs, and Trade Marks; 32nd Report of the Comptroller General for 1914.* [H.C. 160.] Price 2½d.

THE number of applications for patents in 1914 was 24,820 compared with 30,077 in 1913, and 15,036 patents were sealed, as against 16,599 in the preceding year. To the end of the year, 250 applications for avoidance or suspension of patents were made, under the temporary Acts of 1914. Licences were granted, or are to be granted in 172 of these cases, two patents were avoided, and one has been suspended: 20 applications were refused and 39 withdrawn. In 10 cases the applications were returned because the patents had expired, etc., 5 applications are standing over, and one licence under a patent has been avoided.

*German chemical companies; Dividends of —.* Brit. and Col. Drug., April 9, 1915.

THE following announcements have been made by the companies mentioned:—Chemische Fabrik vorm. Goldenberg, Geromont und Co., Winkel, a dividend of 14% for 1914 as in the preceding year; Verein Chem. Fabriken, Mannheim, 12½% as against 20%; Ges. für Chemische Industrie, Gelsenkirchen-Schalke, 8% as compared with 10%; Chem. Werke Lubzysynski und Co., Berlin-Lichtenberg, 10% as contrasted with 15%; Rhein. Gerbstoff und Farbholz Extrakt-Fabrik, Benrath, 16% as against 18%; and the Verein für Chemische Industrie, Mainz, 15% as compared with 22%; in 1913. On the other hand, the Wilhelmsburger Chemische Fabrik, of Hamburg, incurred a loss of £9000 in 1914, this contrasting with a dividend of 10% in the previous year.

*Germany. Prohibited exports.* Chem. and Drug., April 17, 1915.

ACCORDING to a decree of April 1st, the following articles have been added to the list of war requirements the exportation of which from Germany is prohibited: Lycopodium; methyl salicylate (artificial); vegetable gelatin and glue-powder; barium chloride and other barium salts; barium oxide, barium peroxide, and other barium compounds; sulphur chloride; carbon bisulphide; sal ammoniac; ammonia; sodium bicarbonate; salts of nitrous acid; acetic acid, and acetic anhydride; acetates; calcium carbide; sodium sulphide; sulphates; potassium chromate and bichromate; sodium chromate and bichromate; lactic acid; zinc ashes and zinc oxide; malonic acid and its derivatives; sulphites; carbolic acid and its derivatives; calcium phosphide; artificial magnesium carbonate; lead acetate and solution

of lead subacetate. Another decree of April 1st extends prohibition of exportation from Germany to aluminium naphtholdisulphonate (alummol), argentamine (ethylenediamine silver-phosphate solution), silver lactate (actol), silver citrate (itrol), silver-albumin compounds, such as silver proteinate, silver protalbinat, silver nucleinate, sophol (silver formonucleinate), albumose silver, novargan, largin, hegonone, gelatose silver, silver caseinate and sodium silver caseinate, gliadine silver, argyrol, silver sulphochthyolate, colloidal silver; silver nitrate and the fused nitrate, organic and inorganic silver compounds, and preparations thereof which are not mentioned by their names in this decree; perugen (artificial Peru balsam); ointments and pastes made of vegetable, animal, or mineral fats; thallium salts, zinc acetate, zinc permanganate, zinc phenol-sulphonate, zinc sulphate. The prohibition of exportation of kaolin has been revoked.

## Books Received.

*MOLECULAR ASSOCIATION.* By W. E. S. TURNER, D.Sc. Longmans, Green, and Co., 39, Paternoster Row, London. Price 5s.

THIS is the sixth of the series of Monographs on Inorganic and Physical Chemistry, edited by Dr. A. Findlay. The various chapters deal with molecular association in gases; molecular complexity of dissolved substances, molecular complexity in the liquid state and methods for its determination; the molecular complexity of water and the theory of dynamic allotropy; the selection and use of molecular formulae; molecular association and physical properties; molecular association and chemical combination. An appendix of 43 pages contains a summary of the investigations of molecular complexity of dissolved substances. The volume is 8vo, and occupies 170 pages.

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